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TECHNICAL OPERATIONS SUPPORT (TOPS) II
Delivery Order 0014: Improved Thermal Control Coatings

Universal Technology Corporation

OCTOBER 2005
Final Report

AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

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14. ABSTRACT
Alion Science and Technology (Alion) was tasked to support Universal Technology Corporation (UTC), the prime contractor, in conducting detailed technical assessments and analyses of emerging novel research approaches for the Materials and Manufacturing Directorate of the Air Force Research Laboratory (AFRL) at Wright-Patterson Air Force Base, Ohio. As the subcontractor, Alion was tasked to develop improved pigments via exploring new pigments, optimization of pigment particle size, calcinations of pigment, encapsulation of pigment, evaluation of resultant pigments, and scale up of fully formulated coatings. This final report describes our effort to develop improved thermal control coatings.

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PREFACE

Alion Science and Technology (Alion) was tasked to support Universal Technology Corporation (UTC), the prime contractor, in conducting detailed technical assessments and analyses of emerging novel research approaches for the Materials and Manufacturing Directorate of the Air Force Research Laboratory (AFRL) at Wright-Patterson Air Force Base, Ohio. As the subcontractor, Alion was tasked to develop improved pigments via exploring new pigments, optimization of pigment particle size, calcinations of pigment, encapsulation of pigment, evaluation of resultant pigments, and scale up of fully formulated coatings. This Final Report describes our effort to develop improved thermal control coatings.

Respectfully submitted,

Alion Science and Technology

Michael Kenny
Research Chemist
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SECTION 1
INTRODUCTION

1.1 Background

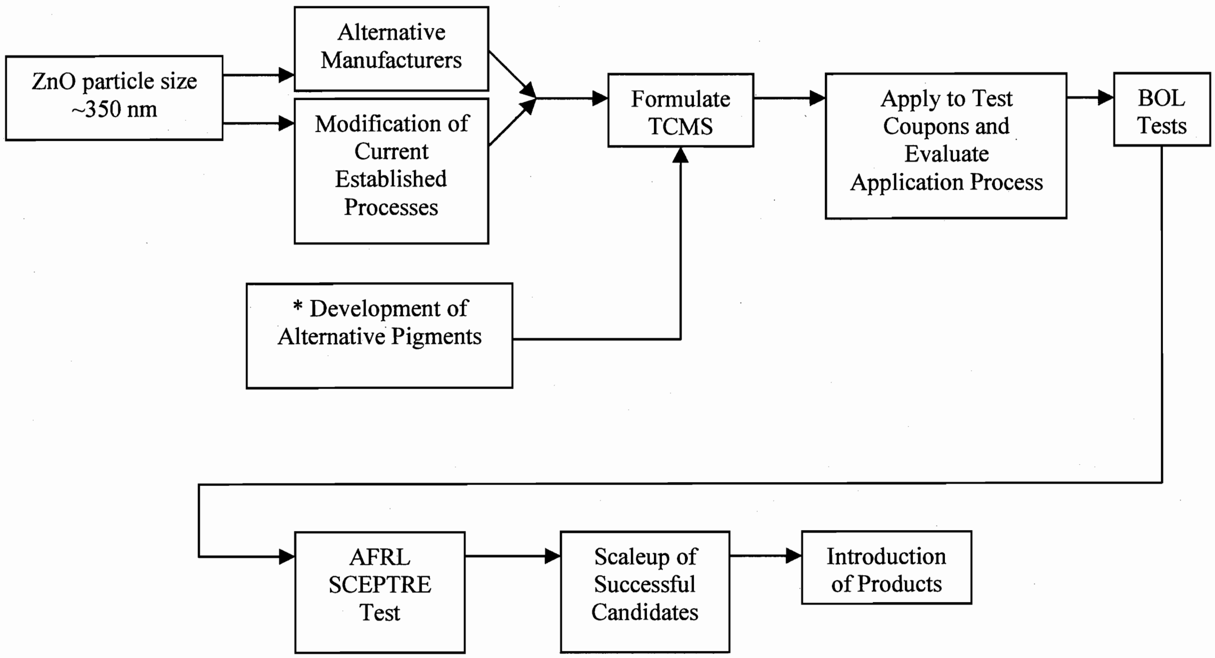
A given spacecraft's thermal management system is in part dependent on the performance of an applied thermal control material system (TCMS). A TCMS degrades over time (e.g. the design lifetime for Z93P is approximately twenty years). Thus, its end of life (EOL) performance may change significantly from its beginning of life (BOL) performance level. In order to compensate for this degradation, the thermal management system may be designed much larger than initially planned. This larger design can potentially add more cost to the overall program.

To account for this degradation, the Advanced Materials and Process Engineering Laboratory (AMPEL) at Alion proposed to develop new TCMSs. These proposed new TCMSs will have improved BOL optical performance, such as solar absorptance and infrared (IR) emissivity, via optimization of their pigment particle size or via development of alternative pigments. This optimization will result in better EOL performance and more efficient designing of the thermal management system. Overall, improved Particle size or the development of new pigments will increase the service lifetime of a spacecraft's thermal management system.

1.2 Study Objective

The main objective of this project was to improve the pigment particle size of zinc oxide (ZnO) and/or to develop new pigments. For ZnO, a particle size of approximately 350 nanometers (nm) will give the most effective diffractive scattering. In this project, a particle size of less than or equal to 350 nm for ZnO is the goal. Figure 1-1 is a schematic diagram of the development of an improved TCMS. Details about the process can be found in our technical proposal.

Figure 1-1. Schematic Diagram of TCMS Development



* The following is a list of "alternative pigments." Some of these "alternative pigments" have been explored in the past and others are new concepts. Alion and AFRL reviewed past data and chose these "alternative pigments" for further study in this program: ZOTP, DZOTP, ZOT, Microspheres, and Nano-ZnO.

1.3 Success Criteria

Table 1-1 below lists the current BOL performance and success criteria for various steps of this project.

Table 1-1. Current Performance and Success Criteria

Areas of Improvement	Current Performance	Success Criteria
Solar Absorptance (silicates)	$\alpha_S \leq 0.20$	$\alpha_S \leq 0.12$
Solar Absorptance (silicones)	$\alpha_S \leq 0.22$	$\alpha_S \leq 0.15$
Emittance (silicates)	$\varepsilon_N \geq 0.85$	$\varepsilon_N \geq 0.90$
Emittance (silicones)	$\varepsilon_N \geq 0.85$	$\varepsilon_N \geq 0.90$
Adhesion/Thermal Shock	ASTM-D-3359A = Pass 4A	ASTM-D-3359A = Pass 4A to 5A
Surface Resistance (for conductive candidates)	$\leq 1 \times 10^{10}$ Ω/□	1×10^{6} Ω/□ to 1×10^{10} Ω/□ (tailorable within the range)
Sprayability and TCMS Quality	Listed in TCMS specifications	Must match current criteria
Torsion Test	Pass/Fail	Pass/Fail

Notes:

α_S = solar absorptance
ε_N = normal emittance
Ω/□ = ohms per square
ASTM = American Society for Testing and Material

SECTION 2

DESCRIPTION OF TEST PROGRAM

2.1 Task 1: Optimization of Pigment Particle Size

Alion optimized the pigment particle size of ZnO in two approaches. In the first approach, Alion evaluated new sources of ZnO using several criteria including purity (greater than 99%), particle size (less than or equal to 350 nm), availability and cost. After evaluating the manufacturers, one source was used for processing. Zinvisible ZnO pigment was chosen due to the familiarity with the manufacturer- Zinc Corporation of America (ZCA). This is same manufacturer that produces SP500 ZnO, which is currently used to manufacture two of Alion's heritage coatings- Z-93P and S13GP:6N/LO-1. ZCA is an approved source and currently meets all quality standards set by the industry.

For the second approach, Alion modified the processing of the current and accepted source of ZnO in an attempt to reduce particle size. The source of this ZnO is the Zinc Corporation of America; they produce SP500 ZnO with a purity of 99.99% and a surface mean diameter of 300 nm to 500 nm. Decreasing the particle size of ZnO and/or reducing agglomeration can be achieved through the following methods. Note that each TCMS produced had particle size measurements conducted by AFRL.

1) **Grinding the raw ZnO using mechanical means such as crushing (mortar and pestle), and grinding the new pigment using various amounts of media, different shapes of grinding media and varying grinding durations. The type of media (hardness) will be the same throughout the process, and the speed of the roller will not vary.**
2) **Varied the grinding duration of formulated TCMS at three different durations (two hours, four hours and six hours).**

After production of the appropriate size pigment particle, the following steps will occur for Task 1:

1) **All promising pigment candidates were used to formulate a TCMS (10-gram to 400-gram batch sizes).**
2) **Each TCMS was ball-milled, and the appropriate physical properties (e.g. density and viscosity) were measured.**
3) **Each TCMS was applied onto 6061 aluminum substrates via spray deposition and cured appropriately.**

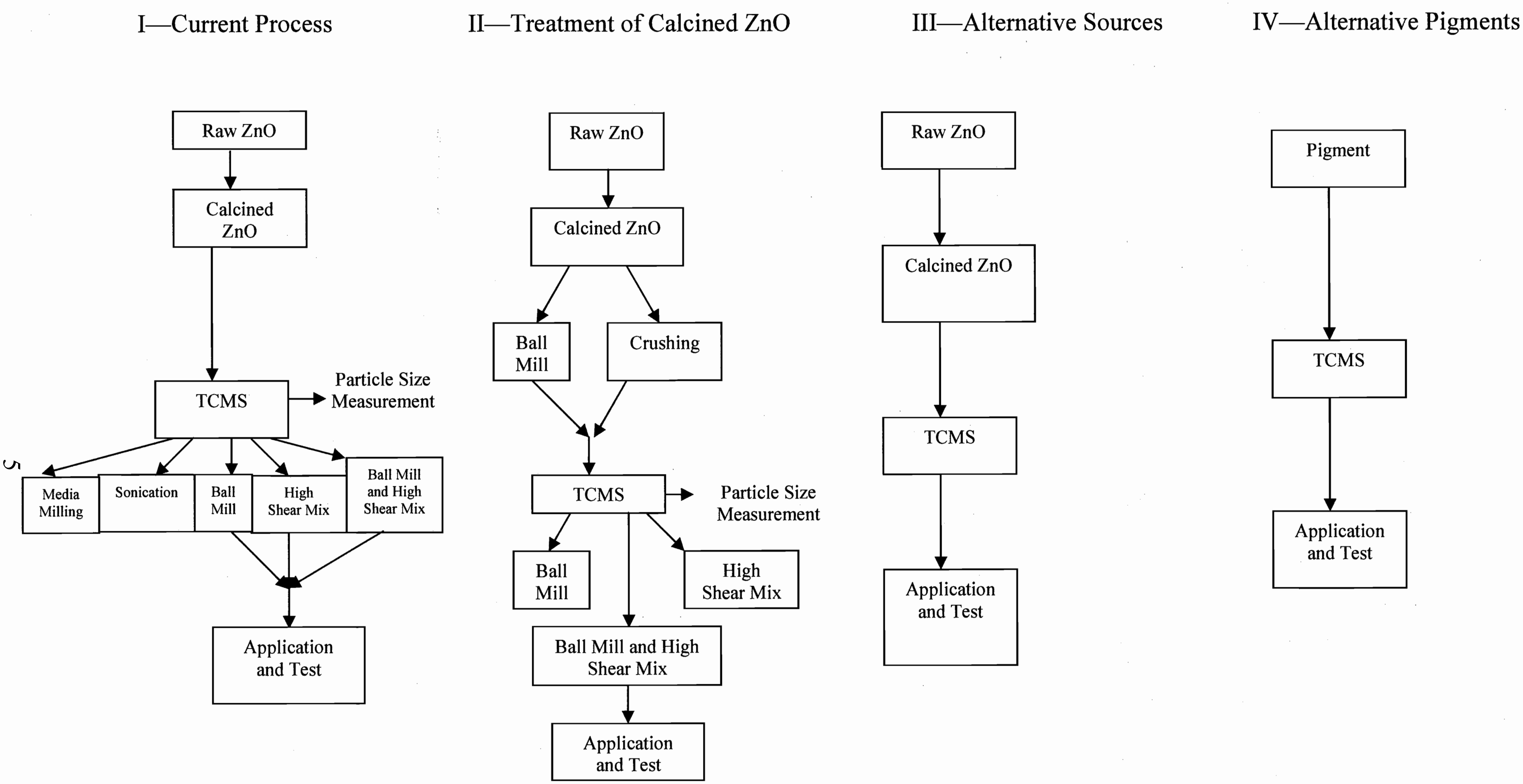


Figure 2-1. Four Steps of the Procedure

2.2 Task 2: Encapsulation of Pigment

The uncalcined Zinvisible pigment was microencapsulated via existing procedures with potassium silicate or hybrid doped silicate. The goal of this step is to develop a pigment for organic white coatings comparable to S13GP:6N/LO-1.

2.3 Task 3: Development of Alternative Pigments

Alion investigated new pigments that had a potential for a high refractive index, such as doped zinc-ortho-titanate (D-ZOT) and ZOT-P (commercial) (see Figure 1-1 for full list).

2.4 Task 4: Evaluation of Resultant Pigments

The 6061 aluminum substrates coated with TCMSs and cured in Task 1 through Task 3 will be evaluated and characterized for the following BOL tests:

1) **Standard operating procedure (SOP) C-AMCL-007, "Measuring Hemispherical Reflectance," using a Lambda 9 ultraviolet/visible/near infrared (UV/VIS/NIR) spectrophotometer with an integrating sphere**
2) **SOP C-AMCL-008, "Measuring Total Normal Emittance," using the Gier-Dunkel DB100 method**
3) **SOP C-AMCL-018-01, "Torsion Test for Coating Adhesion Evaluation"**
4) **SOP C-AMCL-030, "Resistivity Measurements Using the Hewlett Packard 4339A High Resistance Meter for surface Resistance Measurements."**
5) **SOP C-AMCL-040, "Adhesion Testing of Coating," per ASTM D3359**
6) **SOP C-AMCL-046, "Testing Thermal Shock Stability of Coatings."**

2.5 SCEPTRE Testing at AFRL

A total of 29 separate formulations were created for this project. A total of 44 separate batches of material was formulated, sprayed and tested. Of these, 7 formulations (3 baseline) were submitted for the final 1000 SCEPTRE test. The basis for choosing this was the performance each showed in BOL testing at Alion and a previous SCEPTRE test performed earlier in the program.

SECTION 3

RESULTS AND DISCUSSIONS

3. Results and Discussions

3.1 Baseline Materials

With the goal of this research being "Improved Thermal Control Coatings", the engineering assessment can only be fruitfully made by comparing the new suggested concepts with carefully prepared "heritage" materials that are currently state-of-the-art Thermal Control Material Systems (TCMS). Since newer concepts are designed as variations on the existing base materials and processes, the baseline TCMS manufacturing, sample preparation and characterization were first undertaken.

The baseline white (low αs/€n) formulation was straight forward. Alion produces a variety of white TCMS' that are fully qualified for use in the Aerospace industry. For this study, the baseline materials are Z-93/Z-93P, Z-93C55, YB-71/YB-71P and S13GP:6N/LO-1. Z-93/Z-93P, Z-93C55 and YB-71/YB-71P are water-based inorganic white ceramic TCMS (Z-93/Z-93P, Z-93C55 are ZnO based white; YB-71/YB-71P are zinc-ortho-titanate (or ZOT) based), S13GP:6N/LO-1 is a flexible white organic Coating.

3.1.1 Material Processing

All baseline materials were processed using, SOPs, material specifications, process specifications and best established practices developed at Alion. Each formulation was sprayed onto 6061 aluminum plates of various dimensions. Each was also deposited on glass substrates for use by AFRL.

The inorganic TCMS's need high humidity during deposition and initial one day cure. The balance of the cure consists of a clean laboratory environment at ambient conditions.

Table 3-1 Baseline Materials

Material	Pigment	Binder
Z-93	Calcined ZnO	Kasil Potassium Silicate + DI Water
Z-93P	Calcined ZnO	PS-7 Potassium Silicate + DI Water
Z-93C55	Flash Calcined ZnO doped with Indium Hydroxide	Hybrid Silicate + DI Water
YB-71	ZOT	PS-7 Potassium Silicate + DI Water
YB-71P	ZOT	Kasil Potassium Silicate + DI Water
S13GP:6N/LO-1	Micro-encapsulated ZnO	Polymethyl-disiloxane

3.1.2 Characterization

The samples were characterized for optical performance was well as adhesion. The optical properties were characterized by measuring the total hemispherical spectral reflectance and the total normal emittance. The measurements followed that best practices listed as SOPs at Alion. The measurement of total hemispherical spectral reflectance was carried out on a Lambda-19 Spectophotometer, using an integrating sphere. The spectral reflectance was used to calculate solar absorbance via the recommended ASTM method (ASTM-E-490). The total normal emittance (ε) was calculated by subtracting the observed DB-100 reading from one. Adhesion is based on ASTM-D-3349A X-cut method.

The data generated on optical properties for base-line materials were measured and are provided in table 3.2. S13GP:6N/LO-1 data (from random samples of current inventory) has $\alpha = 0.18$ and $\varepsilon = 0.90$.

Table 3-2 Results of Optical and Adhesion characterization for Baseline Concepts

Material	Batch # and Board ID		Alpha (α)	Emittance (ε)	ASTM-D3359A Adhesion Rating	Notes
Z-93	B-555	AA	0.13	0.91	4A	New Ball Mill
	B-557	AB	0.14	0.91	4A	Old Ball Mill
Z-93P	B-548	RA	0.12	0.92	4A	New Ball Mill
	B-549	RB	0.12	0.92	4A	Old Ball Mill
	B-608	AI	0.14	0.92	4A	4 hr. Ball Milling
	B-607	AH	0.12	0.92	4A	ZnO crushed to fine powder
	C-328	BC	0.12	0.92	4A	
	C-756	CF	0.12	0.91	4A	SCEPTRE Sample
	C-758	CG	0.12	0.91	4A	SCEPTRE Sample
YB-71	B-559	AC	0.12	0.90	4A	6 mils
	B-569	AE	0.1	0.92	4A	7mils
	B-582	AG	0.09	0.90		Z-93P Primer 8 mils
YB-71P	B-560	AC	0.11	0.89	4A	
	B-571	AF	0.11	0.90	4A	
	C-767	CK	0.08	0.90	4A	SCEPTRE Sample
	C-765	CJ	0.08	0.90	4A	SCEPTRE Sample
Z-93C55	C-215	SL	0.13	0.90	4A	

3.2. Ball Milling Experiments

3.2.1. Long Duration Ball Milling

In some Aerospace companies' specifications, the duration for ball milling is in the range of 4 to 6 hours. Through previous research, we at Alion, have determined that the longer an inorganic water-based TCMS is milled does not equate to particle size reduction or optical performance. The results displaced in table 3-2 show the result of minor changes in ball milling procedures. We used a "new" ball mill (broken in per Alion SOP) vs. our 8 year old ball mill. The optical properties were identical. We also used a motar and pestle to crush calcined ZnO in an effort to reduce agglomerates. The crushed material was smoother and had less agglomerates for deposition, but the optical properties were unchanged.

The noticeable difference in optical properties was evident from the batch that had a 4 hour ball milling duration vs. our standard 1 hour. Upon initial visual observation, you can see yellowing on the substrates. This translated to a higher solar absorptance (0.14 vs. 0.12). From this exercise, we concluded that there is no noticeable advantage to the long duration ball milling. On the contrary, there is a detrimental effect either from grinding media contamination or an effect on the interstitial properties of ZnO.

3.3 Nanomaterials

3.3.1 Nano-ZincOxide

One of the primary goals of our research was to reduce the particle size of ZincOxide (ZnO) so as to, theoretically, increase the light scattering effects of ZnO and thus create better BOL properties in the critical wavelength range of 250 nm to 2500 nm. It was surmised that the smaller particle size would lead to more efficient light scattering and bring the solar absorptance (α) from the Z-93P standard of 0.11 to 0.15, to 0.08 to 0.12.

After an extended literature search on nano-ZnO pigments, Alion concluded that the current manufacturer of SP500 ZnO (used in Z-93P and S13GP:6N/LO-1) offered the product with the most potential. Zinc Corporation of America (ZCA) produces both SP500 and a nano-ZnO called "Zinvisible Nano-Fine Zinc Oxide." Zinvisible offers advantages over other nano-ZnO such as: ZCA is an approved source in the aerospace industry, readily available and is an "in-stock" item for ZCA, good traceability documentation, high parity (99.9% ZnO), and inexpensive cost is slightly greater than SP500). Cost is a big factor since, if Zinvisible is qualified, the predicted cost would parallel Z-93P's.

3.3.2 Zinivisible Calcination

With the manufacturer now chosen for nano-ZnO, the process of formulation TCMS's was initiated. The obvious starting point was the calcination process. Stabilization of Zn interstitial in ZnO matrix is key. We, at Alion, have been doing this routinely for decades using the methods reported in previous research and qualification projects. The use of such treated ZnO pigments that have been proven stable in 1,000 ESH exposures can also be used to form coatings with Silicate binders.

For this research we employed our standard calcining process and our standard flash calcining process regarding the Zinvisible ZnO. The initial attempt at calcining appeared successful. The ZnO seems to have lost volume and became more compact. The ZnO also had a yellowish color upon removal from the Calcining oven, as does SP500. The yellowing SP500 overall appeared to dull in color for four days upon returning to full white. The Flash Calcining result ran parallel to the Calcining effort.

3.3.2.1 TCMS Formulation using Calcined Zinvisible

As with the calcining process, it seemed logical to create a TCMS with established formulas incorporated in our current TCMSs'. As the deposition proceeded, a total of nine (9) separate formulas of pigment to binder ratios were explored. Table 3-3 displays the formulas.

Table 3-3 TCMS Formulas Using Zinvisible Nano-ZnO

Formula #	Calcined ZnO Pigment (g)	Kasil 2130 (ml) Potassium Silicate	DIH2O (ml)	Notes
1	300	184	191	Standard Z-93P Formula
2	300	184	341	Increased Water Content
3	300	230	290	Increase Water and Kasil
4	200	250	120	Increase Kasil decrease Water
5	200	230	150	Modify Formula 4 slightly
6	250	250	200	Increase water from Formula 4
7	275	260	300	Increase Kasil and Water decrease pigment
8	300	184	191	50/50 mixture Z-93P + Formula 1
9	300	184	191	75/25 mixture of Formula 1 + Z-93P

Table 3-4 displays the BOL properties of the 9 formulations as measured by Alion.

Table 3-4 Alion BOL Measurements of Promising Nano-ZnO Formulations

Formula #	ε	α	ASTMD-3359 Adhesion	Thermal Shock Results	Notes
1	0.94	0.13	2A=Powdering	Pass	Adhesion is Poor
2	0.94	0.13	2A=Powdering	Pass	Poor Adhesion
3	0.94	0.13	4A=Pass	Pass	No visible flaws
4 4	0.93	0.15	4A=Pass	Pass	Appears Siliceous
5	0.93	0.18	4A=Pass	Pass	
6	0.93	0.13	3A	Pass	
7	0.94	0.13	3A	Pass	Adhesion is borderline
8	0.93	0.12	4A	Pass	Z-93P Primer
9	0.93	0.13	4A	Pass	Z-93P Primer
10	0.93	0.14	2A=Fail	Pass	PS-7 silicate

Based on the results in Table 3-4, the Zinvisible formulation with the most promise were submitted to the AFRL for space simulation testing at the SCEPTRE Facility for preliminary measurements. Table 3-5 displays the result of the Zinvisible Formulas with Z-93P as a baseline, from experiments run in April.

Table 3-5 SCEPTRE Measurements of Promising Nano- ZnO Formulations April 2004

Zinvisible Formula #	BOL α	EOL α	BOL ε	Δ α	Sample Thickness
3	0.119	0.135	0.911	0.016	7.0
1	0.133	0.153	0.913	0.020	5.5
3	0.139	0.154	0.915	0.015	5.5
4	0.151	0.179	0.904	0.028	5.6
10	0.162	0.176	0.915	0.014	4.5

(PS-7)					
Z-93P	0.130	0.147	.0898	0.017	8.0

USAF SCEPTRE TEST 04QV01 Environment
287 hours of Exposure

Solar Environment: **Approximately 2.7 EUVS (~ 775 ESH)**

	Electron Flux	
1 keV Electrons	3.0×10^9	$e^-/cm^2/sec$
10 keV Electrons	6.0×10^9	$e^-/cm^2/sec$
Total Electron Fluence	1.0×10^{16}	$e^-/cm^2/sec$

Specimen Temperature 19-33 C (66-92°F)

Vacuum Pressure $\sim 10^{-7}$

See Appendix 1 for Data

3.3.2.2 Final Samples for final SCEPTRE Evaluation of nano-ZnO Z-93P clones

Based on the results from April 2004 SCEPTRE testing, the USAF/AFRL and Alion decided to produce the best possible samples of the most promising nano-ZnO Z-93P clones. Best established practices, and all knowledge gained from previous nano-ZnO TCMS production employed in this study, were used to produce final samples for SCEPTRE evaluations. Formula 3 (see Table 3.1) was chosen, as well as a baseline Z-93P (2 batches each). The samples were produced in June 2005. The results are in Appendix B. The results showed no real improvement over Z-93P. Test 006 and 011 were Z-93P specimens and had a change in Solar Absorptance of 0.038 after 1012 hours of exposure. The nano-ZnO specimens had 0.053 change in solar absorptance after 1012 hours of exposure (tests 004 and 008). Table 3-6 summarizes the data.

Table 3.6 Final nano-ZnO and Z-93P Samples 1000 Hrs SCEPTRE Exposure

Formula	Alion BOL α	AFRL BOL α	AFRL EOL α (1012 Hours exposed)	ALION BOL ε	AFRL Δα
Z-93P Batch 1	0.120	0.112	0.150	0.90	0.038
Z-93P Batch 1	0.120	0.109	0.147	0.90	0.038
Nano-ZnO Formula 3 Batch 1	0.130	0.145	0.197	0.93	0.052
Nano-ZnO Formula 3 Batch 2	0.132	0.137	0.190	0.93	0.053

Z-93P Batch 2	0.120	0.114	0.159	0.90	0.045
Z-93P Batch 2	0.120	0.112	0.150	0.90	0.038

3.3.2.3 Summary of nano-ZnO Formulations as clones of Z-93P TCMS

The use of nano-ZnO in the formulations of a TCMS parallel to Z-93P was not as straight forward as one would anticipate. The nano-ZnO is very fine powder. This fineness does not lend itself to traditional ceramic TCMS formulations, like the current materials produced by Alion. No linear relationship was definable. It came down to starting with known formulas and tweaking them through established laboratory practices.

The results of the space simulation exposure test shows that the nano-ZnO TCMS is not yet an improvement, in terms of α properties, over the heritage TCMS Z-93P. The BOL solar absorptance is slightly higher, the EOL solar absorptance is higher, and the change in solar absorptance after space simulation exposure is higher. One point of interest is the higher thermal emittance values produced by the nano-ZnO. This can be significant for missions that require higher thermal emittance capacity for a given condition.

The overall performance, however, was promising in terms of optical properties. Minor adjustments in the potassium silicate to water ratio can lead to a formula that performs as Z-93P, with improvement in thermal emittance value.

3.4 Micro-encapsulation of nano-ZnO

The purpose of micro-encapsulation of nano-ZnO was to make a pigment similar to S13G pigment used in S13GP:6N/LO-1, which is a silicone based flexible TCMS with multiple uses. The BOL solar absorptance of S13GP:6N/LO-1 is ~0.18, so there is room for improvement. The traits that make S13GP:6N/LO-1 desirable for space application; flexible, easy to apply and repair, cleanable, AO resistance, low outgassing, would stay the same while we improved optical properties.

Production would start with simulating SP500 micro-encapsulation. Our efforts were launched in pilot scale batches at first. A linear decrease in ingredient weights led to failed encapsulation attempts. The nano-ZnO was too fine for the current production processes. An increase in potassium silicate and higher cook temperature led to a batch that seemed to produce an acceptable pigment. This particular batch was chosen for scale-up to an acceptable production level.

A 25 lbs. batch was produced and used to formulate a TCMS. The TCMS was produced and deposited on aluminum substrates. The TCMS was too powdery for analysis. It was decided the path forward here was not promising enough and the time and effort devoted to producing an S13GP:6N/LO-1 was re-directed to a more productive direction. The pigment seems functional, but the TCMS production will need to be addressed in the future.

3.5 Electrically Conductive Flash Calcined nano-ZnO

The calcining of ZnO for use in Z-93P involves a gradual increase in temperature over time to ~ 650 C. Flash calcining, used to produce our current electrically conductive Z-93P clone named Z-93C55, employs higher temperatures and less dwell time. Our goal was to produce an improved version of Z-93C55, while maintaining all of its properties. The first step was to flash calcine a batch of Zinvisible nano-ZnO as per our standard procedure for flash calcining. The process displayed a product similar to flash calcined SP500.

The resulting flash calcined nano-ZnO was then formulated into a TCMS without the dopant added, so as to ensure that the material had the capability to be deposited readily. Our endeavor produced good sprayability and samples that had BOL solar absorptance values parallel to Z-93C55, but with the higher emittance value (0.93) as seen in other Zinvisible formulations. These encouraging results led to producing samples for inclusion in the final SCEPTRE test. These samples; however, were doped and met the surface resistivity criteria spelled out in Z-93C55 specifications (10^6 to 10^9 ohms per square).

3.5.1 Doped Flash Calcined nano-ZnO.

After successful flash calcinations of the Zinvisible nano-ZnO, the next step was doping the pigment with $In(OH)_3$. The doping process consisted of mixing, water addition (slight pH adjustment), dopant addition, mixing and drying. The process displayed no variations from doping flash calcined SP500. The resultant flash calcined doped nano-ZnO was ready for TCMS formulation.

3.5.2 Doped Flash Calcined nano-ZnO TCMS Production

As a control for our new electrically conductive TCMS, a standard batch of Z-93C55 was produced, sprayed and submitted for inclusion in the final SCEPTRE test. The materials used were from the current inventory at Alion and chosen randomly.

The TCMS formula for the doped nano-ZnO was the same as used for standard Z-93C55. No variations were experimented with. As with the previous Zinvisible formulations, adhesion was good to the substrate, but exhibited some powdering. This did not eliminate its inclusion for testing in the final SCEPTRE (OSQV03) test. The name given for the new formulation was Zinvisible K-C55. The results are included in Table 3-7.

Table 3-7 Doped Nano-ZnO Final SCEPTRE Results Test 05QV03

Formula	Alion BOL α	AFRL BOL α	AFRL EOL α (1012 Hours exposed)	ALION BOL ε	AFRL $\Delta\alpha$
Z-93C55	0.138	0.147	0.187	0.90	0.040
Zinvisible K-C55	0.130	0.123	0.173	0.93	0.050

The results in Table 3.7 would confirm the value of the Z-93C55 as a fundamentally sound product for use in the aerospace industry. The Zinvisible K-C55 proved to be intriguing and would lend itself to follow up work to address the adhesion issue. It would seem that Zinvisible K-C55 could outperform the commercially available current product at Alion. The fact that only one batch was produced shows the need for follow-up work before a new product is introduced to the marketplace.

3.6 ZOT-P Background, History and Formulation

Alion produces a white pigment for use in its commercially available TCMS YB-71P called ZOT. The name ZOT is an acronym for Zinc-Ortho-Titanate, which is a known pigment for thermal control, as well as common sunscreens. The production of ZOT for use in YB-71P is involved and labor intensive, which is the reason YB-71P cost approximately 5 times as much as Z-93P ($1,200.00 vs. $225.00). The reason YB-71P is attractive is that the materials BOL solar absorptance produces the lowest value of all of our TCMS's (0.08 to 0.11). The EOL values are the subject of great debate. There can be a batch to batch variability that can produce EOL values similar to Z-93P or values up to 0.30. The problem lies in controlling the valence of titanium during processing. As seen in Table 3-2, YB-71/YB-71P had BOL solar absorptance values of 0.08 to 0.12, which were lower than Z-93P values of 0.12 to 0.14. Our goal was to eliminate any questions about batch to batch variability as well as reduce the cost of a new ZOT based TCMS by at least 50%.

3.6.1 YB-71/YB-71P Baseline

Before moving on to improving YB-71P, it was necessary to produce quality, consistent batches of YB-71/YB-71P. Table 3.2 shows the result of 7 separate batches of YB-71/YB-71P with consistent results. All of those batches were produced with material chosen randomly from Alion's inventory. These in-house materials will be subsequently used for producing SCEPTRE samples.

3.6.2 ZOT-P Development

In 2000, Alion submitted various samples for use in a space simulation test at AFRL. We had been eager to improve YB-71P, and toyed with a new concept called ZOT-P. the ZOT-P sample performed better than expected, but had sprayability problems. Using this encouraging data as a catalyst, we proposed the material for evaluation in this study.

The key to ZOT-P is in the relative ease with which it is made, compared to YB-71P. Degussa makes an off the shelf precursor ingredient called Titanium Dioxide P-25 that contains the titanium compound in the correct valence. We just have to do a final mix with Alion's precursor and we have Zinc-ortho-titanate or ZOT-P in this case. The labor is reduced 75%.

The resultant ZOT can be made into a YB-71P clone TCMS, which we will call ZOT-P. The formula was to be tweaked since first produced in 2000, so as to produce reproducible sprayability. Four formulas were made into TCMS and are shown in Table 3.8

Table 3-8 ZOT-P Formulations

Formula #	α Alion	E Alion	Adhesion	Notes
Original	NA	NA	Pass	1 to 1 PBR
PS-7 Binder	0.11	0.90	Pass	1 to 1 PBR
1	0.09	0.90	Pass	2 to 1 PBR
1A	0.08	0/90	Fail	2 to 1.1 PBR
2	0.10	0.91	Fail	1 to 1.1 PBR
3	0.12	0.89	Pass	1 to 1 PBR Increase Water, reduce Kasil
4	0.08	0.90	Pass/Acceptable	1 to 1 PBR Increase Kasil, reduce Water

After reviewing the above data, we submitted samples from formula 1 , formula 3 , and formula 4 . The test was run in April 2004 simultaneously with samples from Table 3.5 under the conditions listed therein. Table 3.9 shows the results with YB-71P sample as a control.

Table 3-9 SCEPTRE Measurements of ZOT-P
YB-71P April 2004 Test 04QV01

Formula	BOL α Alion	BOL ε Alion	BOL α AFRL	EOL α AFRL	Δ α AFRL	BOL ε AFRL
1 Sample 1	0.09	0.90	0.091	0.109	0.018	0.884
1 Sample 2	0.09	0.90	0.096	0.128	0.032	0.884
3	0.12	0.89	0.141	0.157	0.016	0.881
4	0.08	0.90	0.078	0.093	0.015	0.886
YB-71P	0.09	0.90	0.109	0.135	0.026	0.878

USAF SCEPTRE TEST 04QV01 Environment
287 hours of Exposure

Solar Environment: Approximately 2.7 EUVS (~ 775 ESH)

	Electron Flux	
1 keV Electrons	3.0×10^9	$e^-/cm^2/sec$
10 keV Electrons	6.0×10^9	$e^-/cm^2/sec$
Total Electron Fluence	1.0×10^{16}	$e^-/cm^2/sec$

Specimen Temperature 19-33 C (66-92°F)

Vacuum Pressure $\sim 10^{-7}$

3.6.3 D-ZOTP

With the increase in demand for electrically conductive TCMS, the next logical step regarding ZOT-P was to determine if it held the capacity to be doped. Since the development of ZOT-P was still on going, only two attempts were made at doping ZOT-P. The second attempt produced a pigment suitable for inclusion in a TCMS. The formula for the TCMS was the same as formula 3 for ZOT-P. Adhesion was acceptable, solar absorptance was 0.09, emittance was 0.90, and surface resistivity was 10^7 ohms per square. This promising BOL data (measured by Alion) led to the inclusion of a sample for SCEPTRE's final test.

3.6.4 Results for ZOT-P and D-ZOTP From 1000 Hour SCEPTRE Final Test

Final Samples of ZOT-P and D-ZOTP along with YB-71P as a control, were submitted to AFRL for the final SCEPTRE test on this program. The results are in Table 3-10.

Table 3-10. 1000 Hour SCEPTRE Exposure for ZOT-P, D-ZOTP and YB-71P Test 05QV03

Formula	Alion BOL α	AFRL BOL α	AFRL EOL α (1012 Hours exposed)	ALION BOL ε	AFRL Δα
ZOT-P Formula 4 Batch 1 Sample 1	0.09	0.081	0.151	0.90	0.070
ZOT-P Formula 4 Batch 1 Sample 2	0.09	0.085	0.147	0.89	0.062
ZOT-P Formula 4 Batch 2 Sample 1	0.09	0.085	0.163	0.90	0.078

ZOT-P Formula 4 Batch 2 Sample 2	**0.09**	**0.084**	**0.143**	**0.90**	**0.059**
D-ZOTP (ZOT-P C55)	**0.10**	**0.078**	**0.172**	**0.89**	**0.094**
YB-71P Batch 1 Sample 1	**0.09**	**0.078**	**0.187**	**0.89**	**0.109**
YB-71P Batch 1 Sample 2	**0.09**	**0.077**	**0.183**	**0.89**	**0.106**
YB-71P Batch 2 Sample 1	**0.09**	**0.078**	**0.207**	**0.89**	**0.129**
YB-71P Batch 2 Sample 2	**0.09**	**0.083**	**0.198**	**0.89**	**0.115**

3.6.5 Results of ZOT-P, D-ZOTP 1000 Hour Exposure

Table 3-10 clearly shows that ZOT-P performed superiorly to YB-71P in terms of change in solar absorptance after 1000 hours of exposure. In fact, ZOT-P performed slightly better than Z-93P in terms of EOL solar absorptance value (final α average = 0.151 for ZOT-P vs. final α average = 0.1515 for Z-93P). This is a definite improvement over our current ZOT based products and an improvement over Z-93P (factoring in BOL data). The BOL data for all the ZOT based TCMS are superior to ZnO based paints: however, ZOT based TCMS degrade at a slightly higher rate when exposed to the space environment. ZOT-P seems to degrade parallel to Z-93P.

The conductive ZOT based TCMS, DZOT-P, also performed better than YB-71P and very similar to Z-93C55. It's EOL value of 0.172 after 1012 hours of exposure in SCEPTRE will enable aerospace engineers to choose from a wider base of improved products that; most importantly, costs less than half the price of the current products.

4.0 Cost Analysis of Potential New Products

4.1 Raw Materials

One of the goals for this study was to ensure that any new product developed was as cost effective as possible. Following that logic, all materials purchased for this study (Zinvisible, Titanium Dioxide) were less expensive or approximately the same cost as the materials used to produce the current products offered to the aerospace industry for thermal control of space hardware. Besides Zinvisible and Titanium Dioxide, the raw materials and supplies used to produce the novel TCMS's for this study were the same used for Alion's current products. This allows the elimination of the need to review and approve new manufactures and materials. It also allowed for streamlined production times, that also reduces costs. These factors will allow the introduction of the novel formulations in a timely manner.

4.1.1 Nano-ZnO

As previously stated in this report, the choice of nano-ZnO Zinvisible was made with the knowledge that its manufacturer was an approved source. Zinc Corporation of America already produces SP500 ZnO (used in all of Alion's white coatings) and Zinvisible. The cost of Zinvisible is approximately $4.00 more per pound than SP500. The projected cost of any material produced from Zinvisible will be only 5% to 10% more than current

materials. The improvements (if any) from the use of Zinvisible in a TCMS will easily offset the minimal price increase.

4.1.2 ZOT-P and DZOT-P Cost Analysis

The purchase of off the shelf Titanium Dioxide P-25 from Degassa Inc. is a tremendous cost savings for any TCMS using Zinc-ortho-titanate (ZOT) as its pigment. There is an elimination of labor intensive commitment to producing titanium dioxide in the laboratory. P-25 can be mixed with other inexpensively mass produced precursors to make ZOT-P. The ZOT-P then is mixed with the same raw materials used to make Z-93P and YB-71P to form a new, less expensive TCMS. This new TCMS is not only an improvement over YB-71P and Z-93P, it will be less than half the cost of YB-71P. The other benefit is that the ZOT-P TCMS sprays the same way as YB-71P and Z-93P, so there is not a need for a new training overhaul if this material is employed.

D-ZOTP is the conductive version of ZOT-P and also uses the same dopant employed by our current line of white conductive TCMS's. Therefore, DZOT-P will also be less than half the cost of Z-93C55 and YB-71C, our current conductive ceramic white coatings.

A projected cost analysis is shown in Table 4.1

Table 4.1 Projected Cost Analysis of ZOT-P and D-ZOTP

Material	Current Cost	Projected Cost FY 2007
ZOT-P	NA	$400.00 per Kit
D-ZOT P Conductive	NA	$450.00 per Kit
YB-71P	$1,300.00 per Kit	$1,300.00 per Kit
YB-71C Conductive	$1,350 per Kit	$1,350.00 per Kit

5.0 Summary

5.1 Nano-ZnO

The use of nano-ZnO in the formulations of a white, ceramic water based TCMS had some promising results. However overall, there was not an improvement over Z-93P. The adhesion was unreliable, and the formulations (1 to 10) all had some adhesion issues. That may be corrected by continuing to modify the PBR ratios and the make-up of the binder solution itself. The downside is the lack of improvement in the BOL and EOL values of solar absorptance. Nano-ZnO offers no improvement over Z-93P in that area. It does offer improvement however, in the thermal emmittance value. The values measured by Alion showed significant improvement (0.90 for Z-93P to 0.93 for nano-ZnO), and the

AFRL measurements also showed improvement (April 2004 0.90 for Z-93P and 0.92 for nan-ZnO). Therein lies the value for the nano-ZnO product offering a product with higher thermal emittance value can offer an aerospace engineer a viable option.

The development of a flexible silicone based nano-ZnO product was stalled at the TCMS formulation stage.

5.1.1 ZOT-P and D-ZOTP

The most obvious improvement to thermal control coatings came in the area of Zinc-ortho-titanate production. The novel new materials offered improved optical properties, less expensive raw materials (and ultimately a less expensive TCMS) and similar sprayability. The materials production time is reduced by approximately 70%, thereby increasing availability.

6.0 Future Work

The most pressing need in terms of future work lies in the repeating of the efforts for our most promising novel TCMS's and submitting them to one or more separate space simulation laboratories. Aerospace Corporation or GSFC would provide excellent space simulation repeatability for ZOT-P, DZOT-P, and perfected nano-ZnO Z-93P clone. If the results are as positive as SCEPTRE's 1000 hour exposure test, the new materials can be ready for the aerospace marketplace.

The development of a white, flexible, silicone based, nano-ZnO pigmented TCMS is still plausible. The many attempts at micro-encapsulation finally yielded an acceptable pigment for TCMS development, but the exercise needs to be developed further.

Sprayability and adhesion was acceptable, but those properties can be perfected with repetition and documentation. All laboratory processes need to be repeated at least one time so as to produce useable material and process specifications for use by aerospace engineers and technicians.

APPENDIX A
ACRONYMS/ABBREVIATIONS

AFRL	Air Force Research Laboratory
AMPEL	Advanced Materials and Process Engineering Laboratory
ASTM	American Society for Testing and Material
BOL	beginning of life
D-ZOT	doped zinc-ortho-titanate
EOL	end of life
hp	horsepower
IITRI	IIT Research Institute
IR	infrared
nm	nanometer
rpm	revolutions per minute
SOP	standard operating procedure
TCMS	thermal control material system
UTC	Universal Technology Corporation
UV/VIS/NIR	ultraviolet/visible/near infrared
ZnO	zinc oxide
ZOT	zinc-ortho-titanate

APPENDIX B

05QV03

SPECTRAL REFLECTANCE HISTORIES

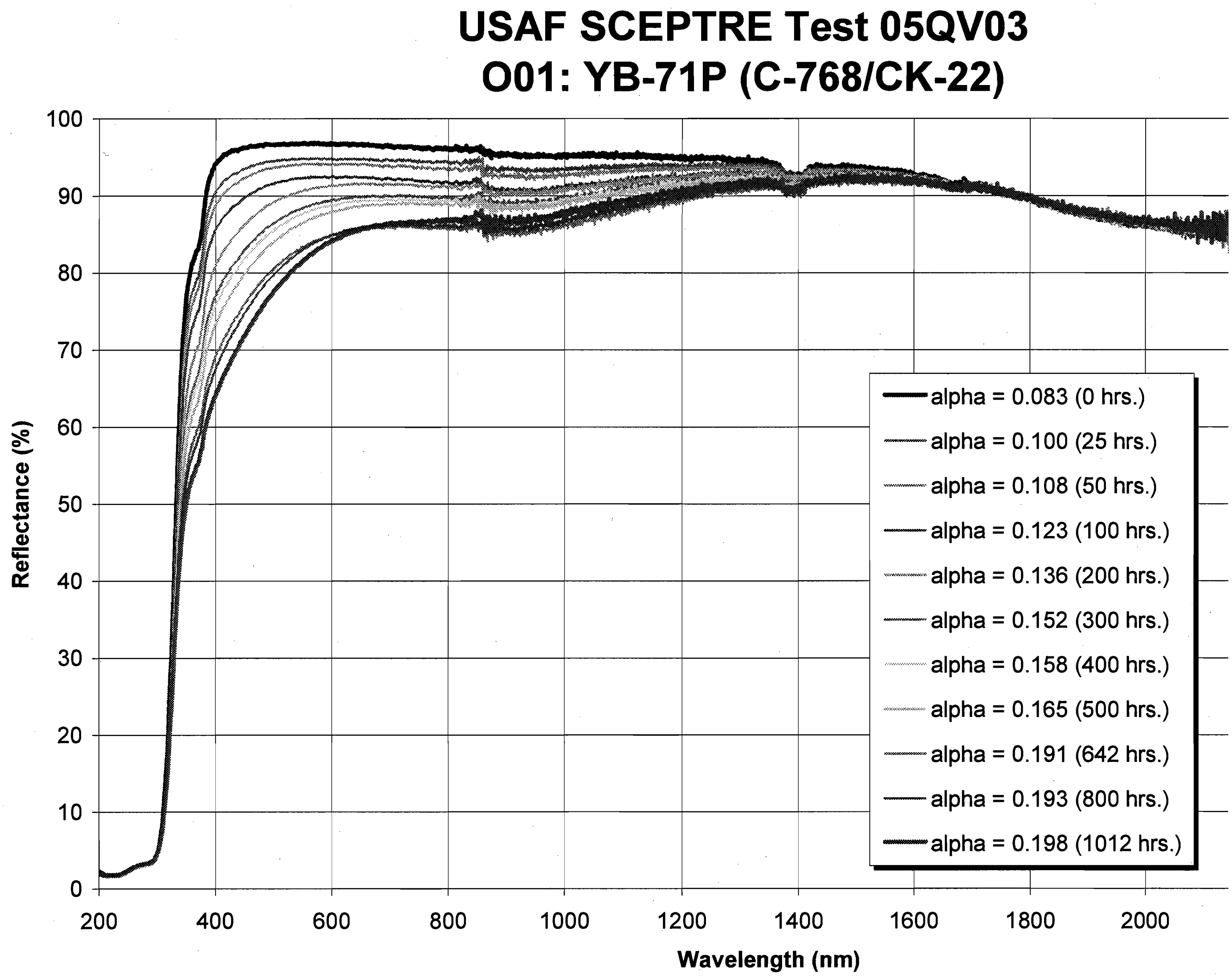


Figure A1. Spectral Reflectance History of Specimen O01: YB71P (C-78/CK-22)

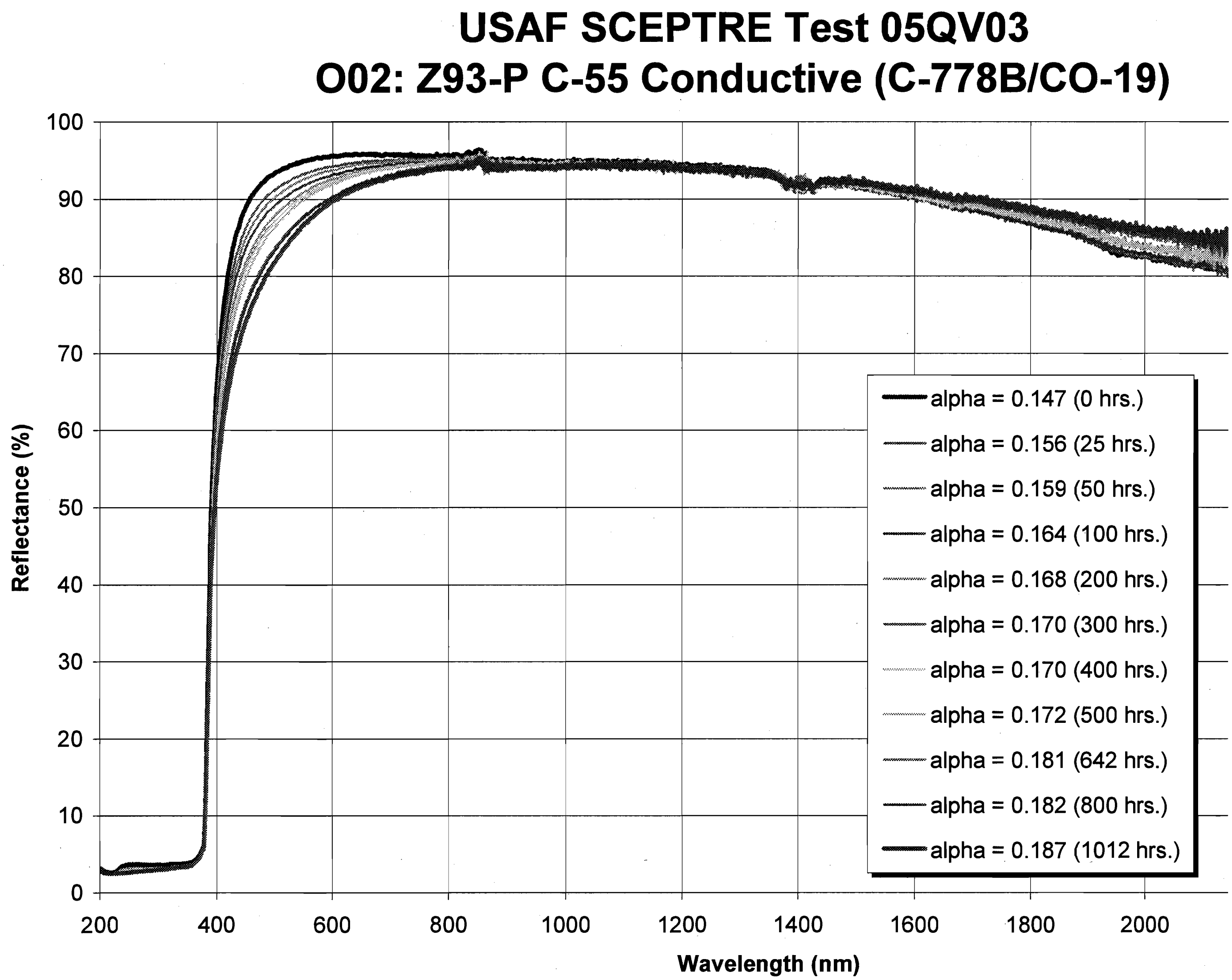


Figure A2. Spectral Reflectance History of Specimen O02: Zinvisible K C55 Conductive (C778/CQ21)

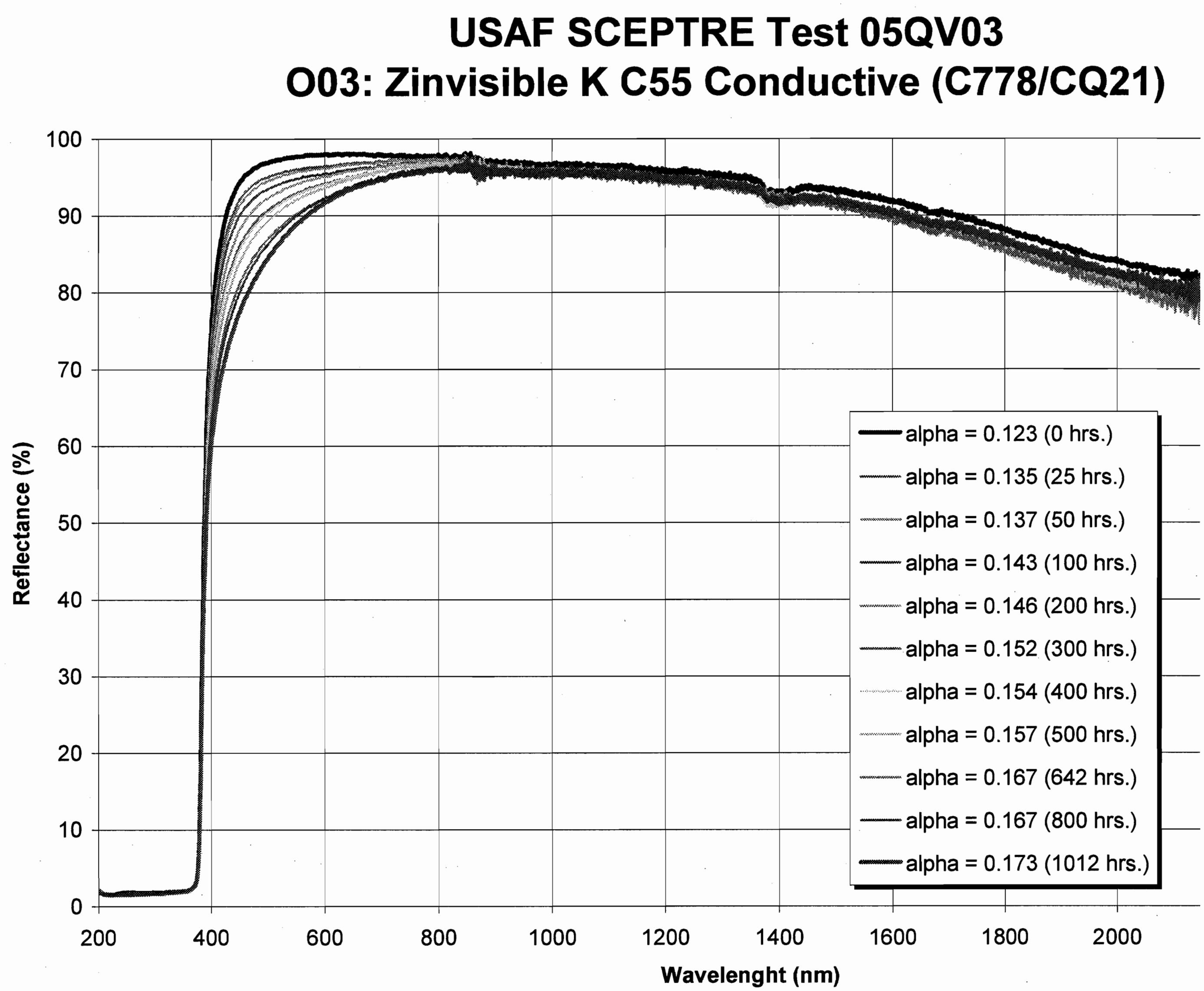


Figure A3. Spectral Reflectance History of Specimen O03: Zinvisible K C55 Conductive (C778/CQ21)

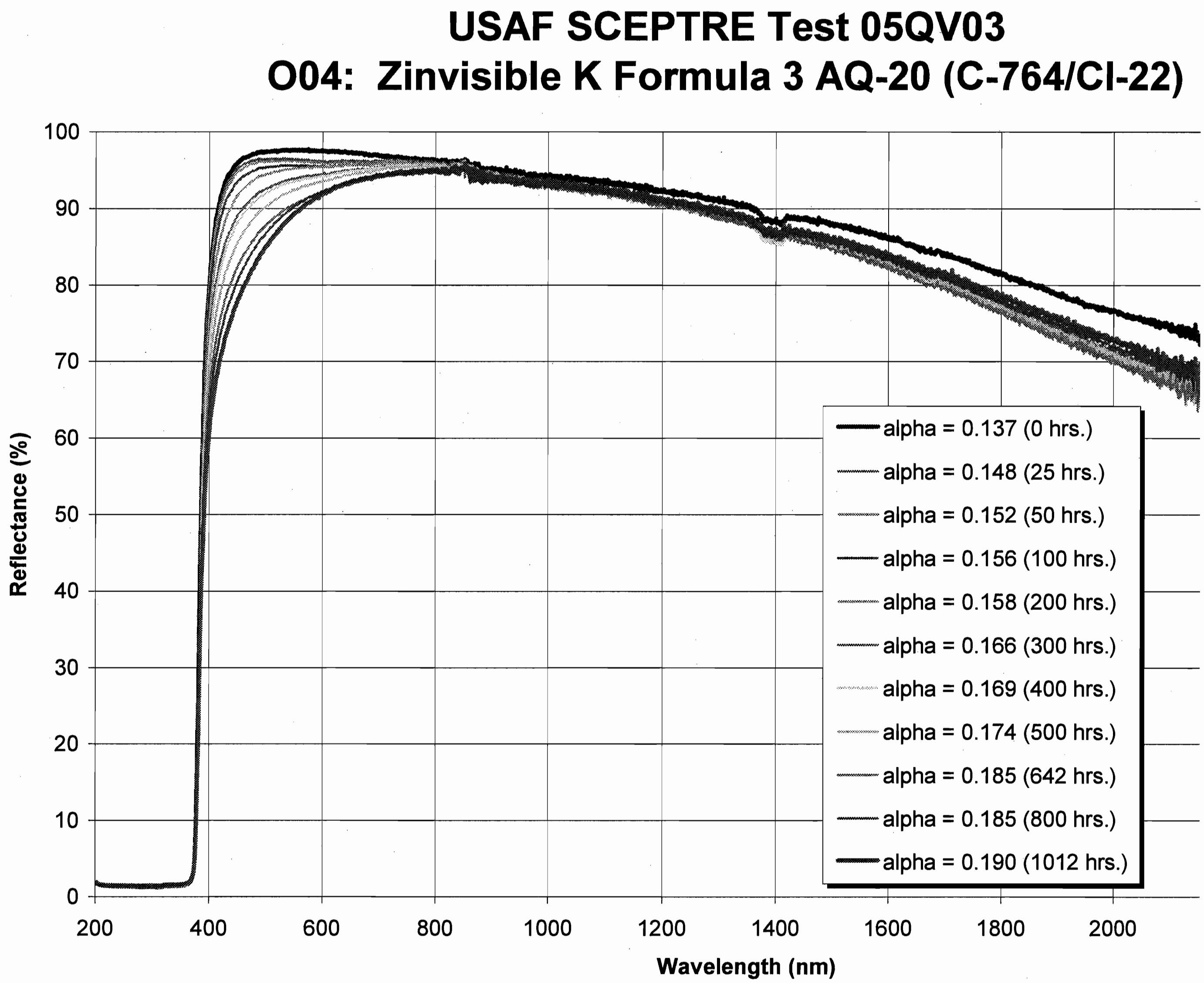


Figure A4. Spectral Reflectance History of Specimen O04: Zinvisible K Formula 3 AQ-20 (C-764/CI-22)

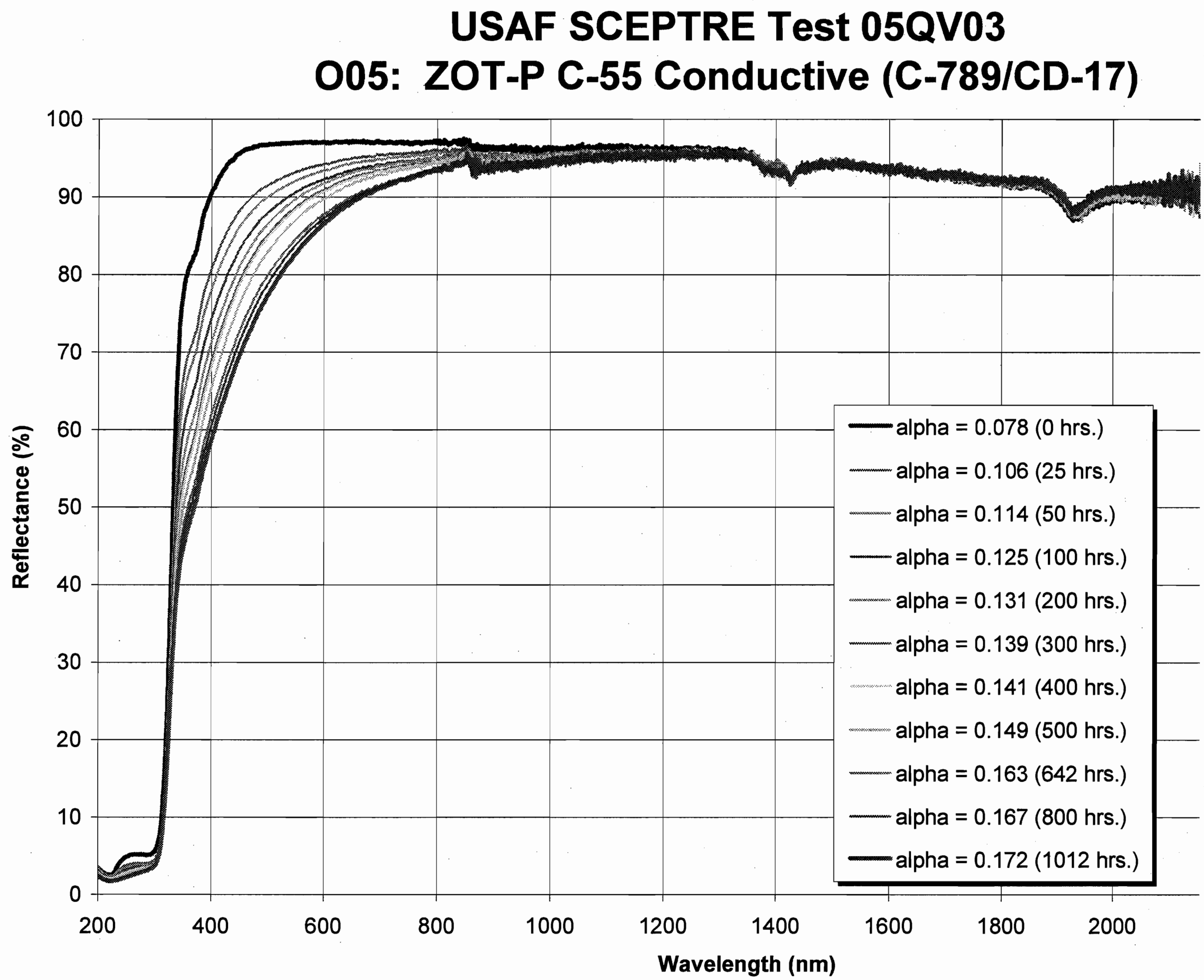


Figure A5. Spectral Reflectance History of Specimen O05: ZOT-P C-55 Conductive (C-789/CD-17)

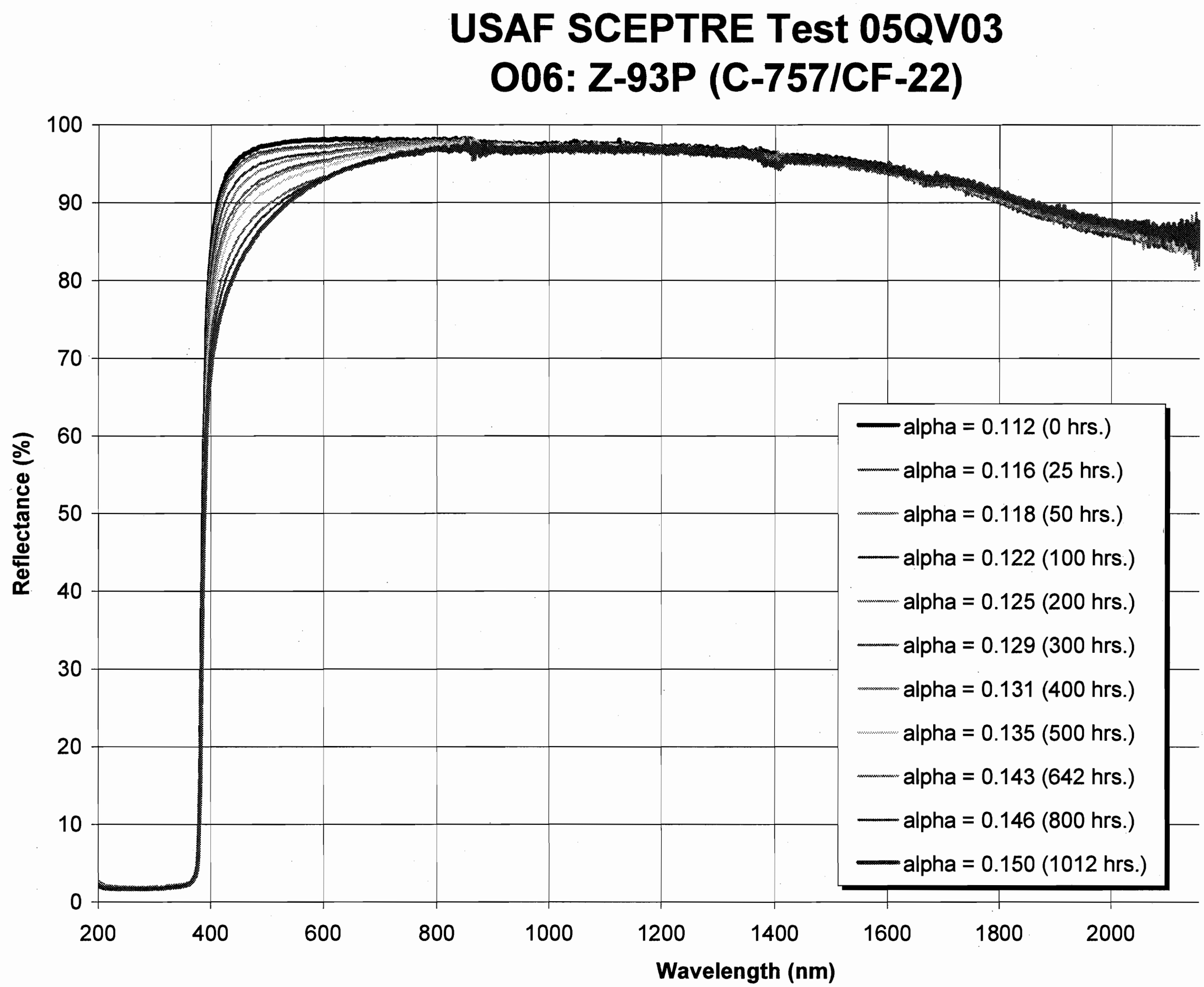


Figure A6. Spectral Reflectance History of Specimen O06: Z-93P (C-757/CF-22)

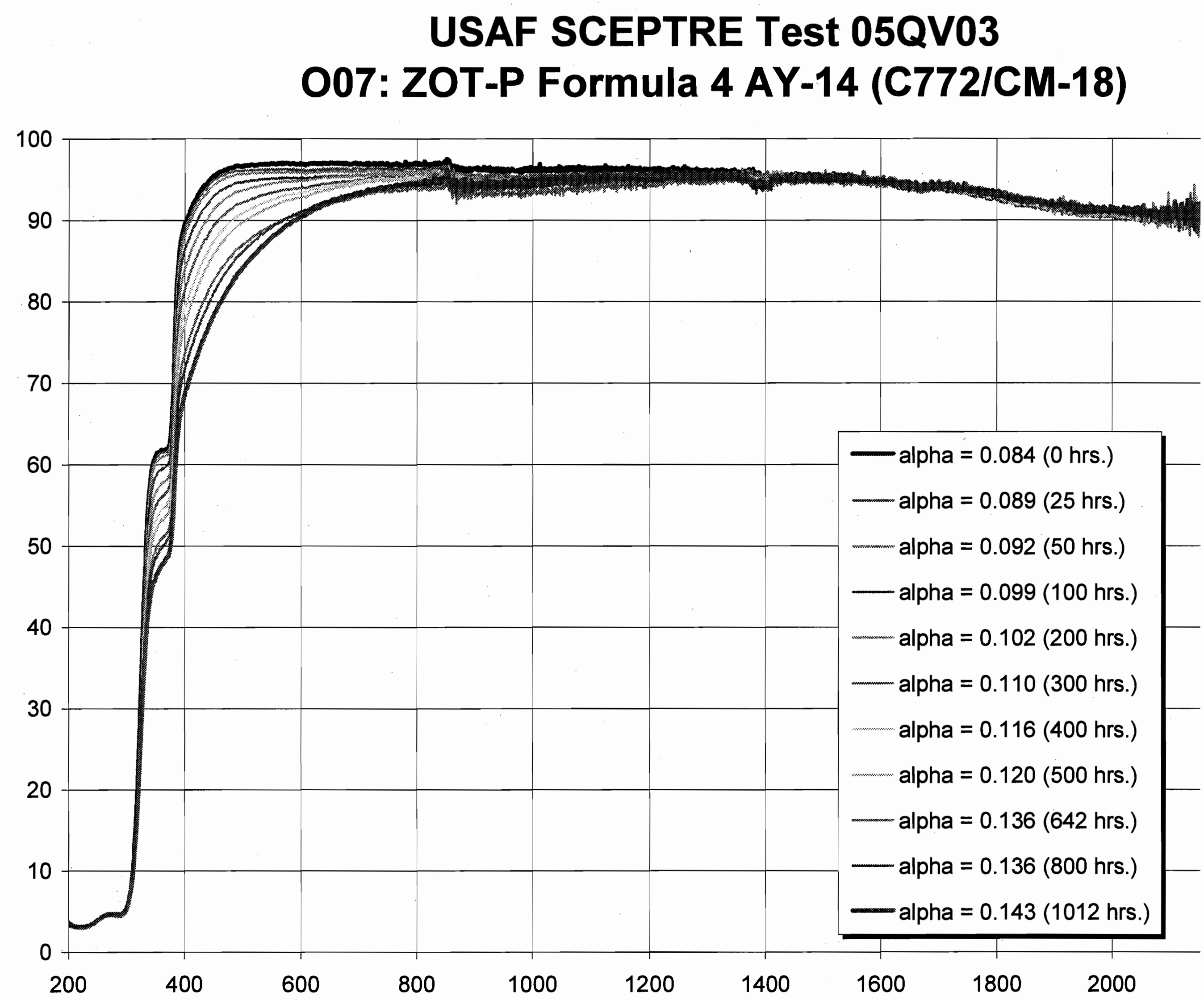


Figure A7. Spectral Reflectance History of Specimen O07: ZOT-P Formula 4 AY-14 (C772/CM-18)

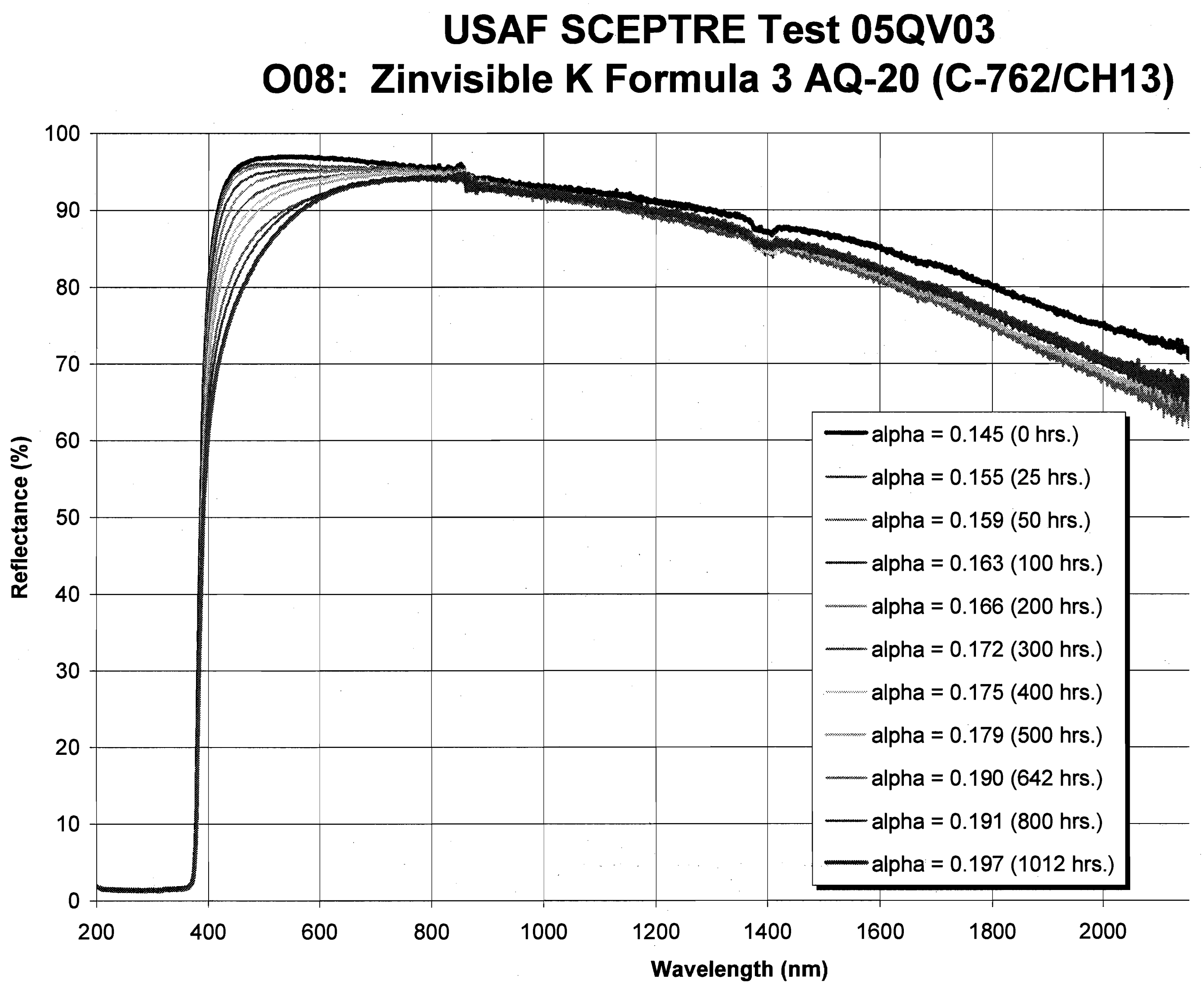


Figure A8. Spectral Reflectance History of Specimen O08: Zinvisible K Formula 3 AQ-20 (C-762/CH13)

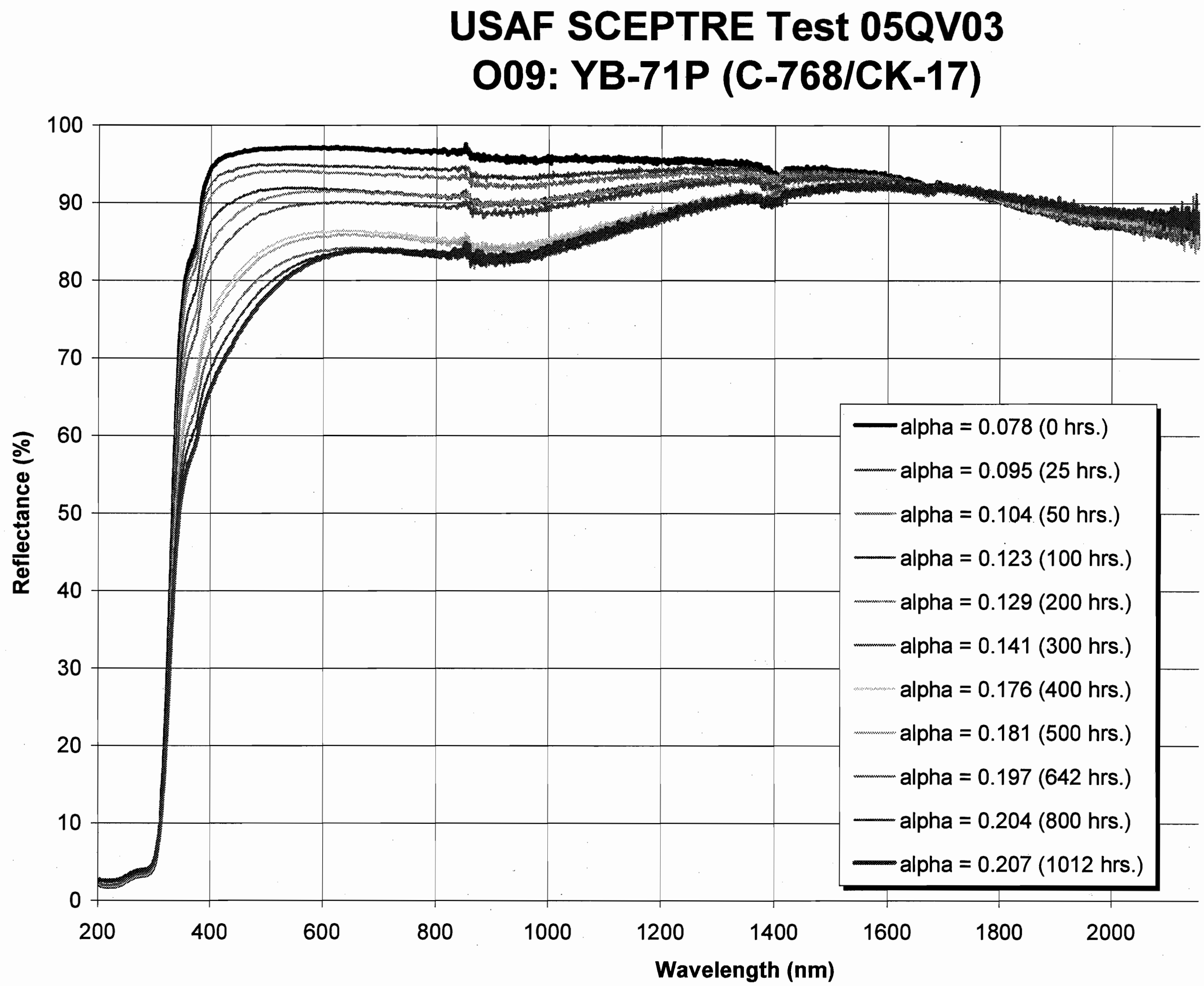


Figure A9. Spectral Reflectance History of Specimen O09: YB-71P (C-768/CK-17)

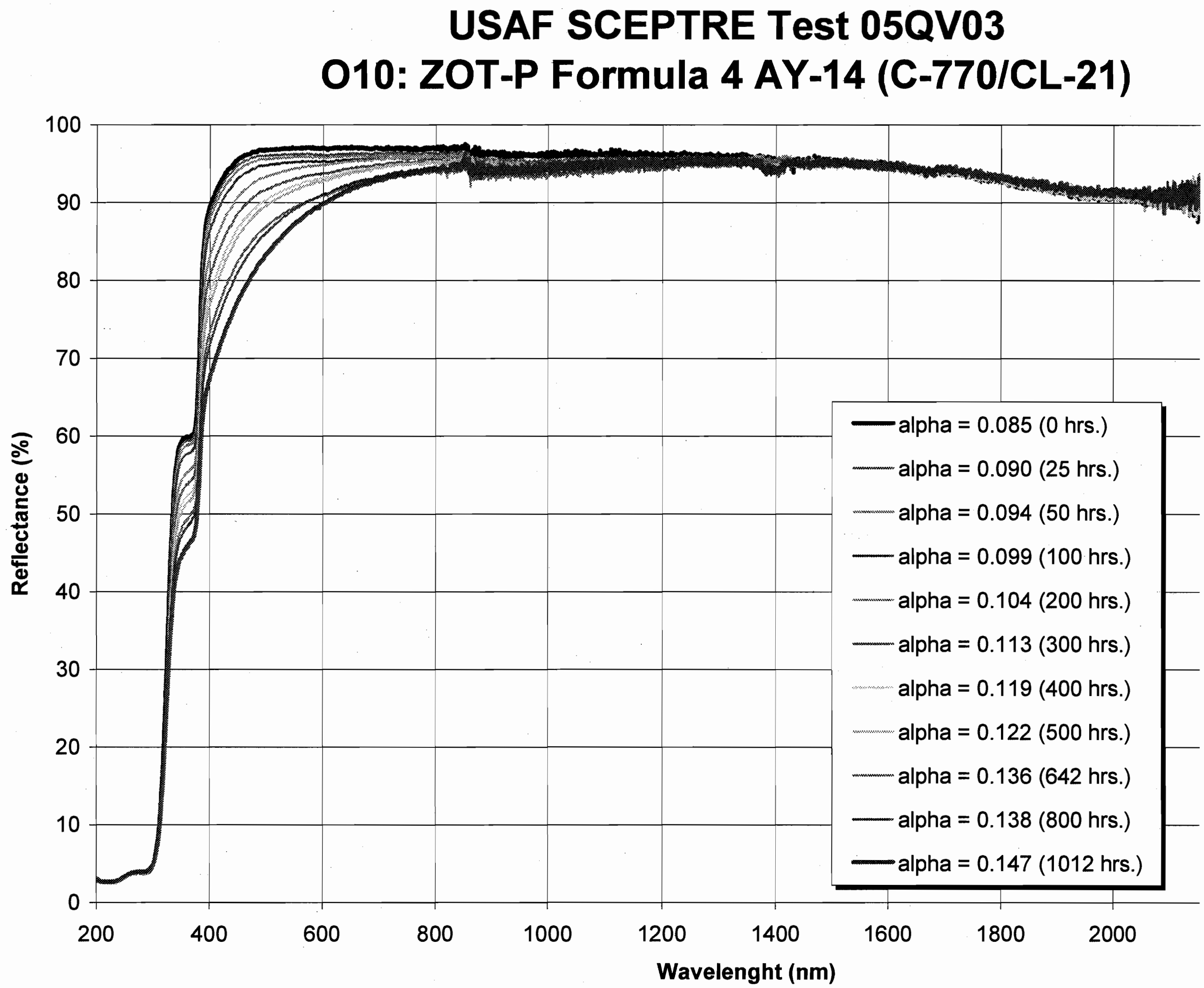


Figure A10. Spectral Reflectance History of Specimen O10: ZOT-P Formula 4 AY-14 (C-770/CL-21)

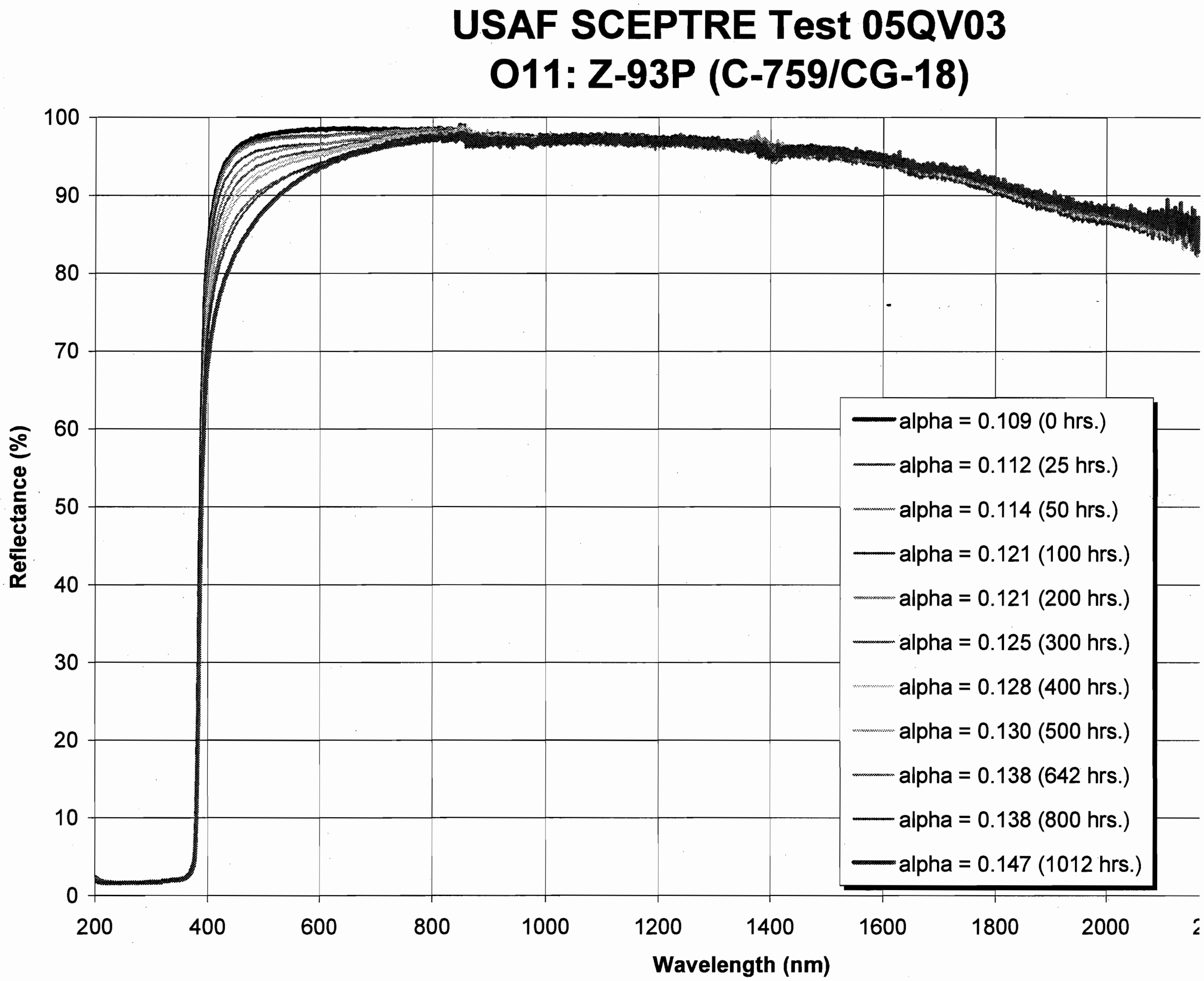


Figure A11. Spectral Reflectance History of Specimen O11: Z-93P (C-759/CG-18)

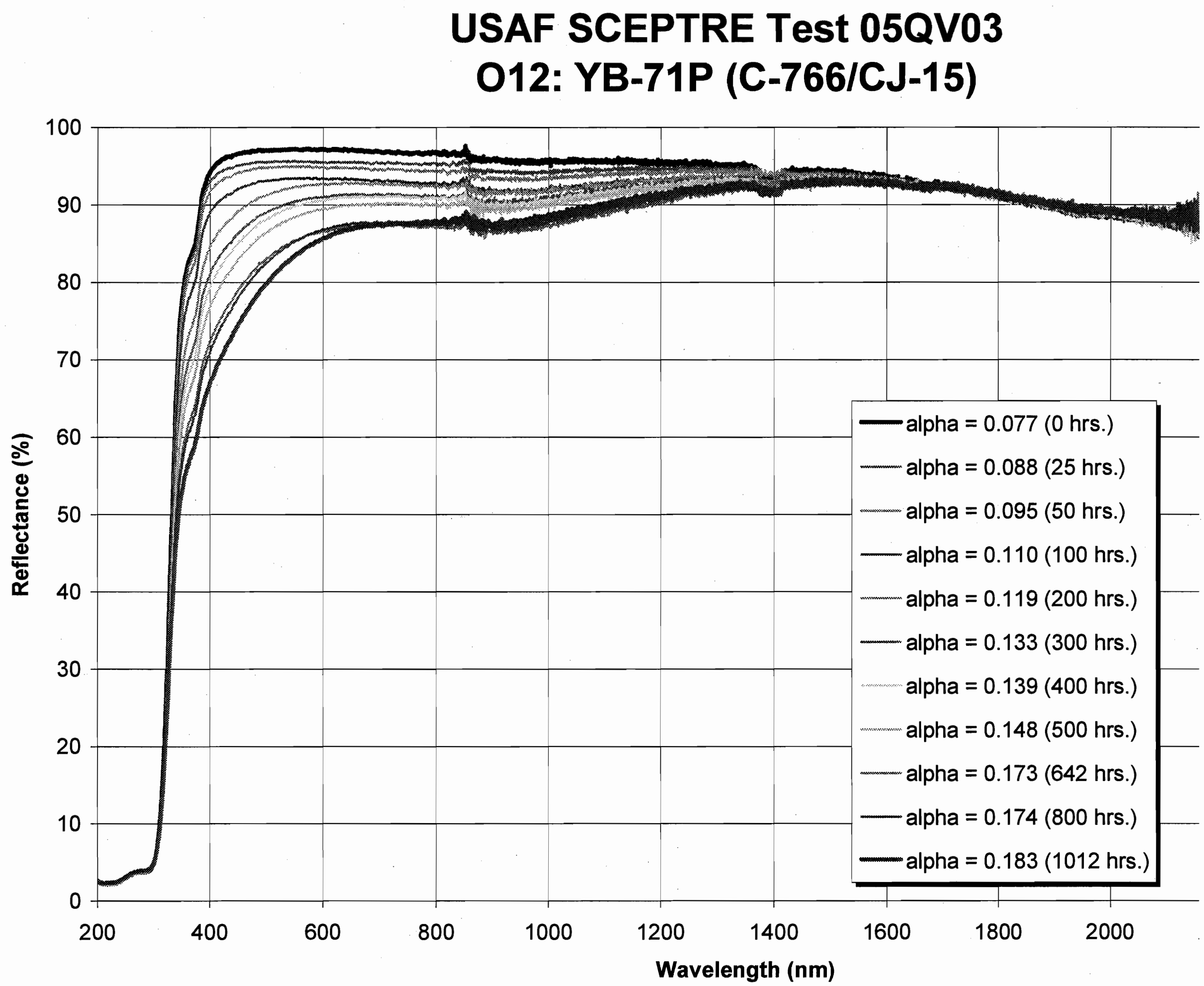


Figure A12. Spectral Reflectance History of Specimen O12: YB-71P (C-766/CJ-15)

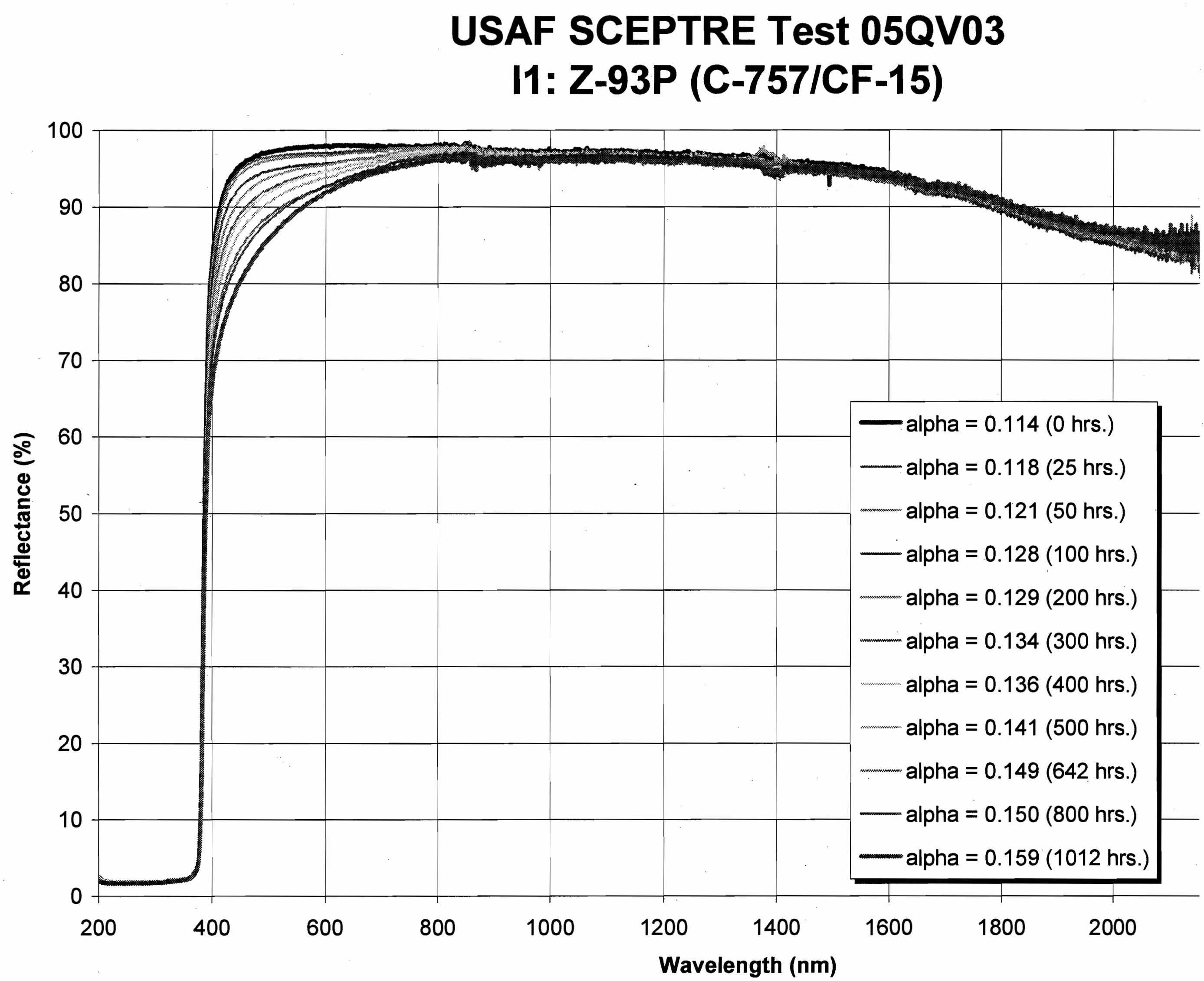


Figure A13. Spectral Reflectance History of Specimen I1: Z-93P (C-757/CF-15)

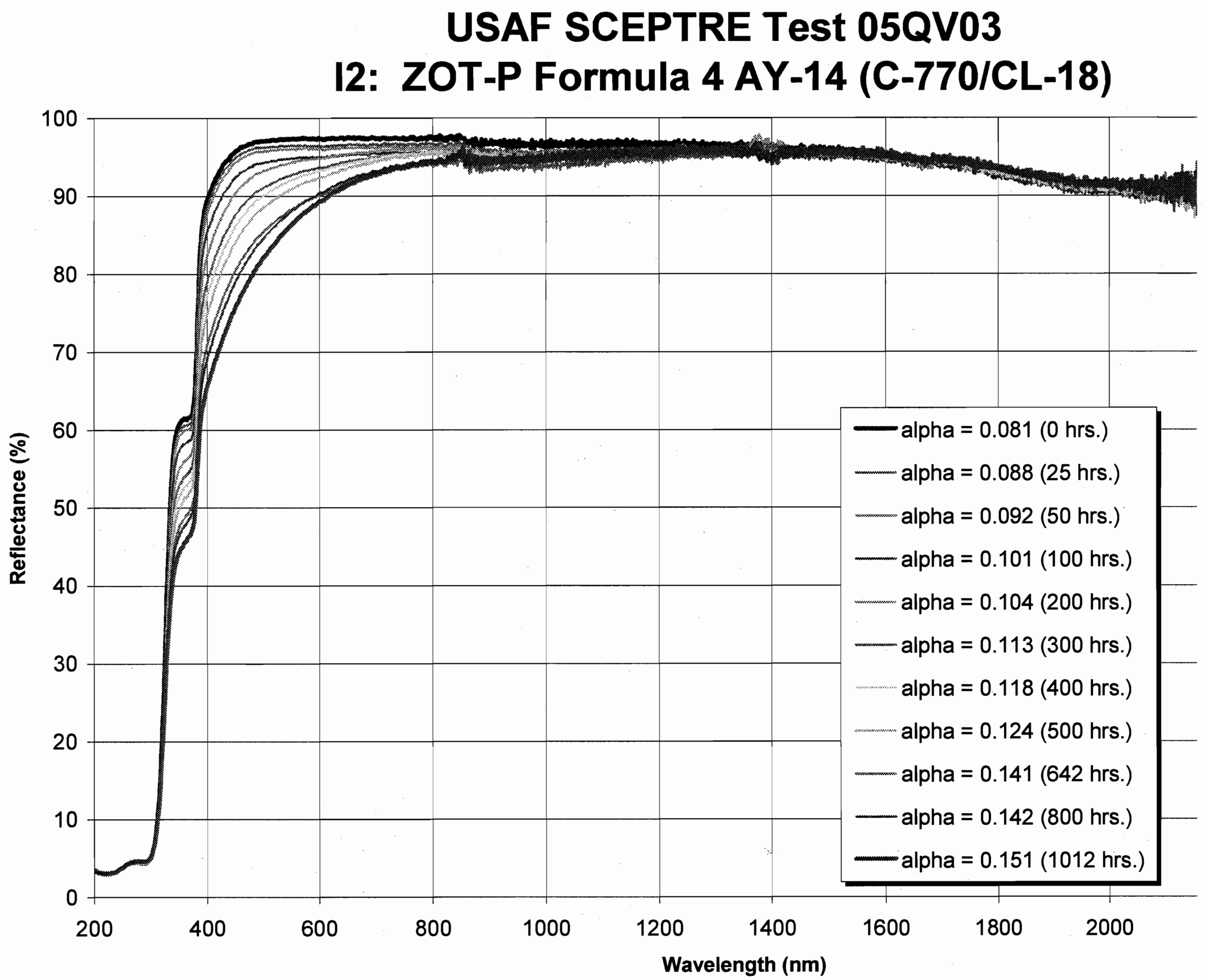


Figure A14. Spectral Reflectance History of Specimen I2: ZOT-P Formula 4 AY-14 (C-770/CL-18)

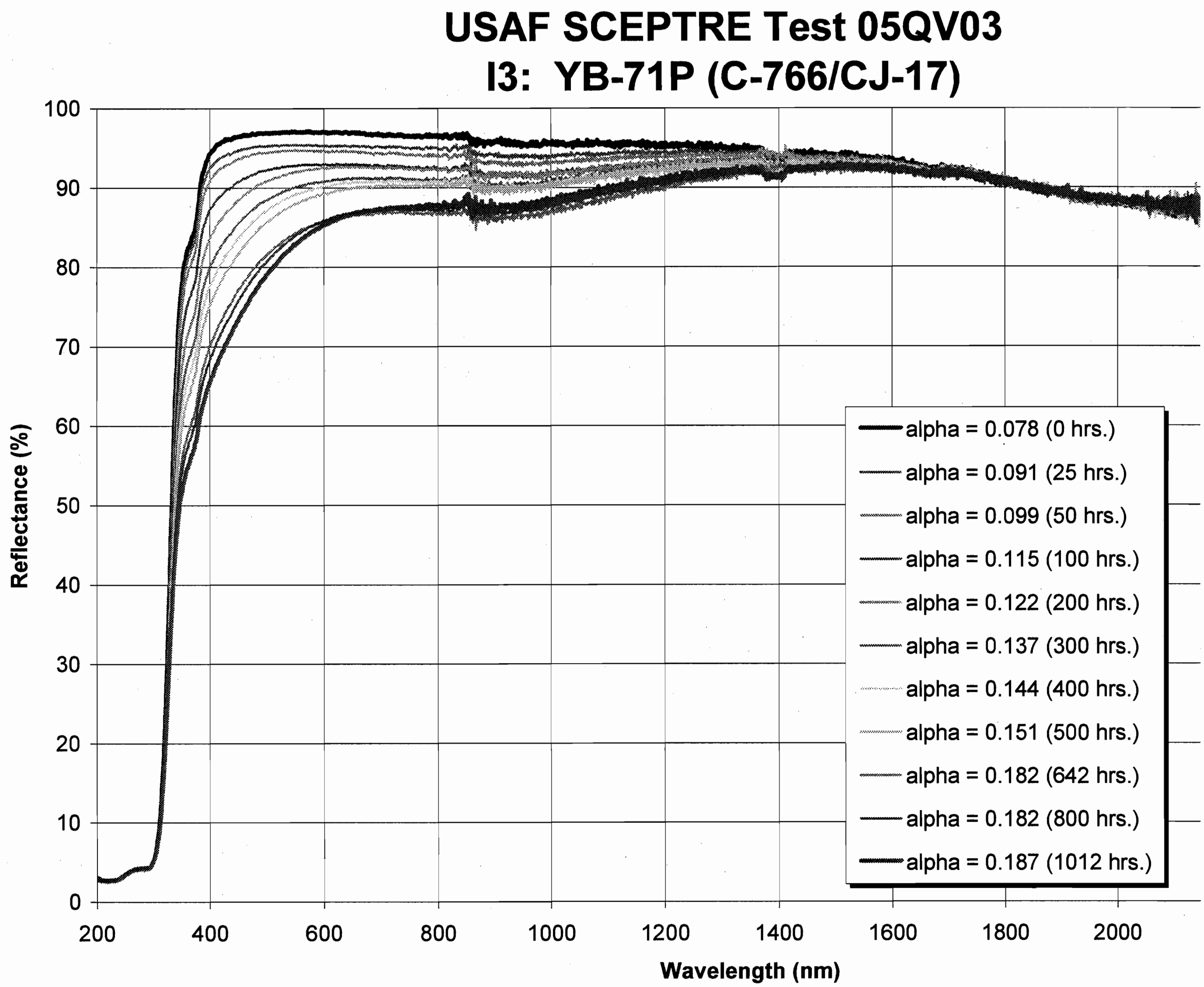


Figure A15. Spectral Reflectance History of Specimen I3: YB-71P (C-766/CJ-17)

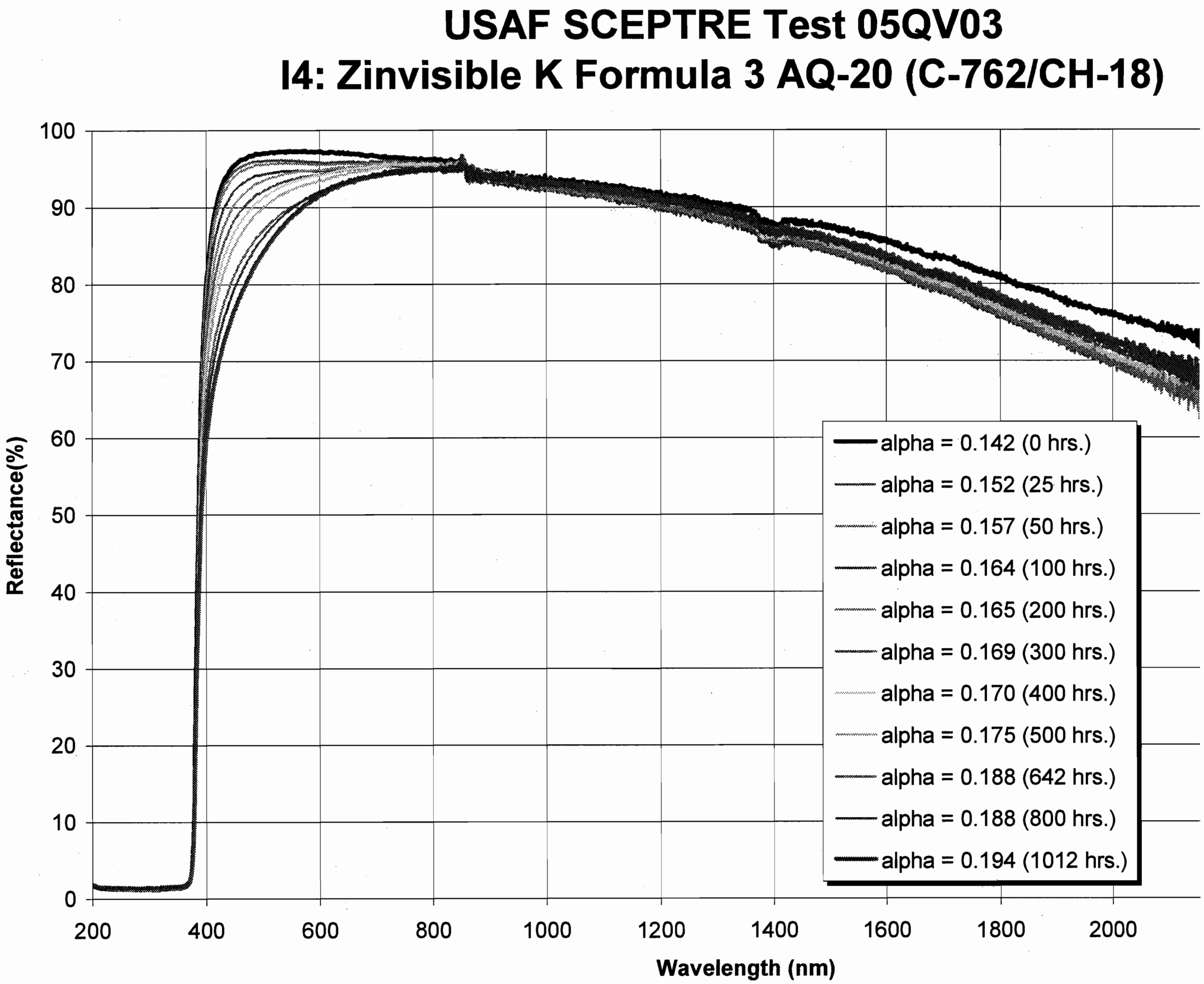


Figure A16. Spectral Reflectance History of Specimen I4: Zinvisible K Formula 3 AQ-20 (C-762/CH-18)

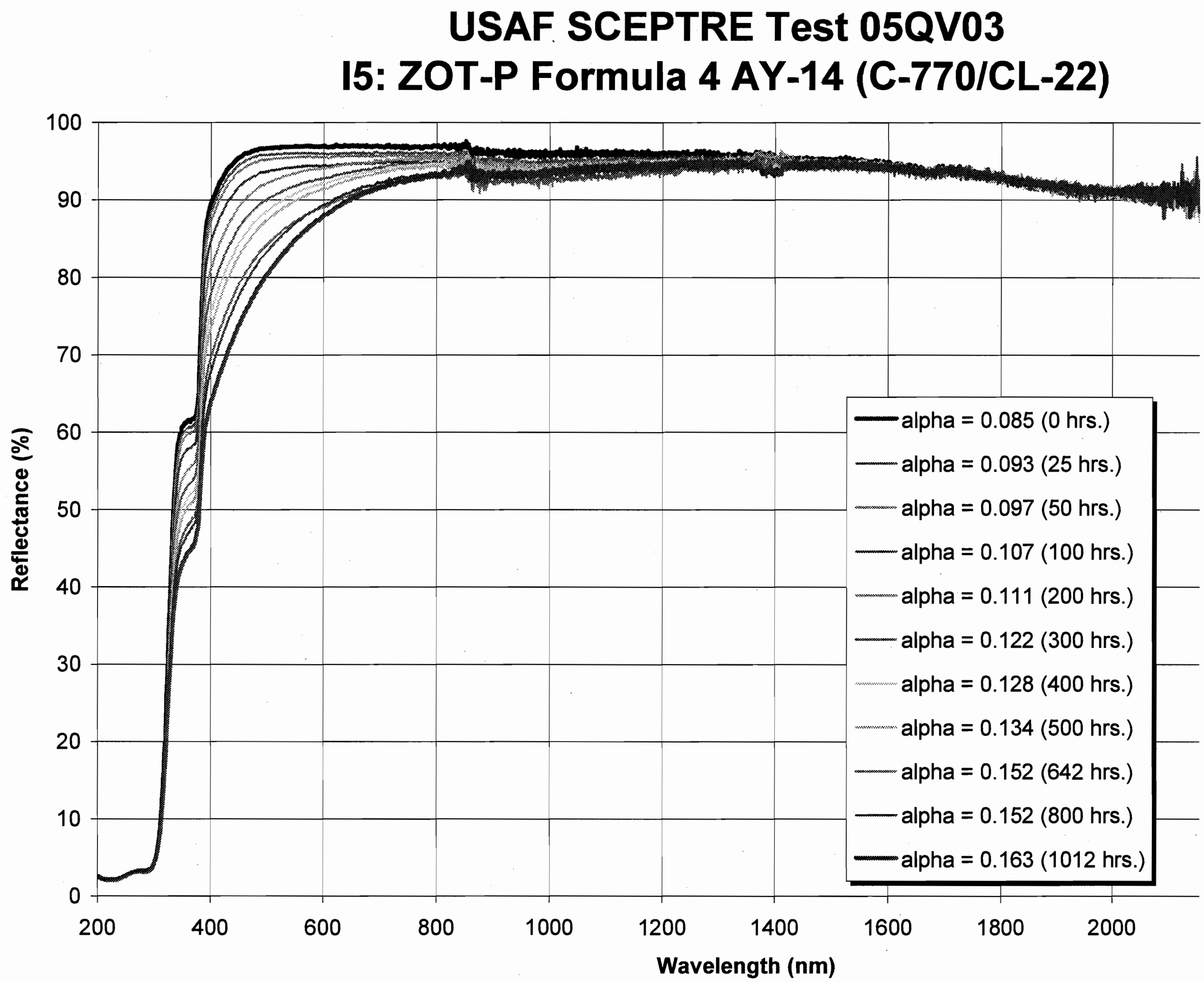


Figure A17. Spectral Reflectance History of Specimen I5: ZOT-P Formula 4 AY-14 (C-770/CL-22)

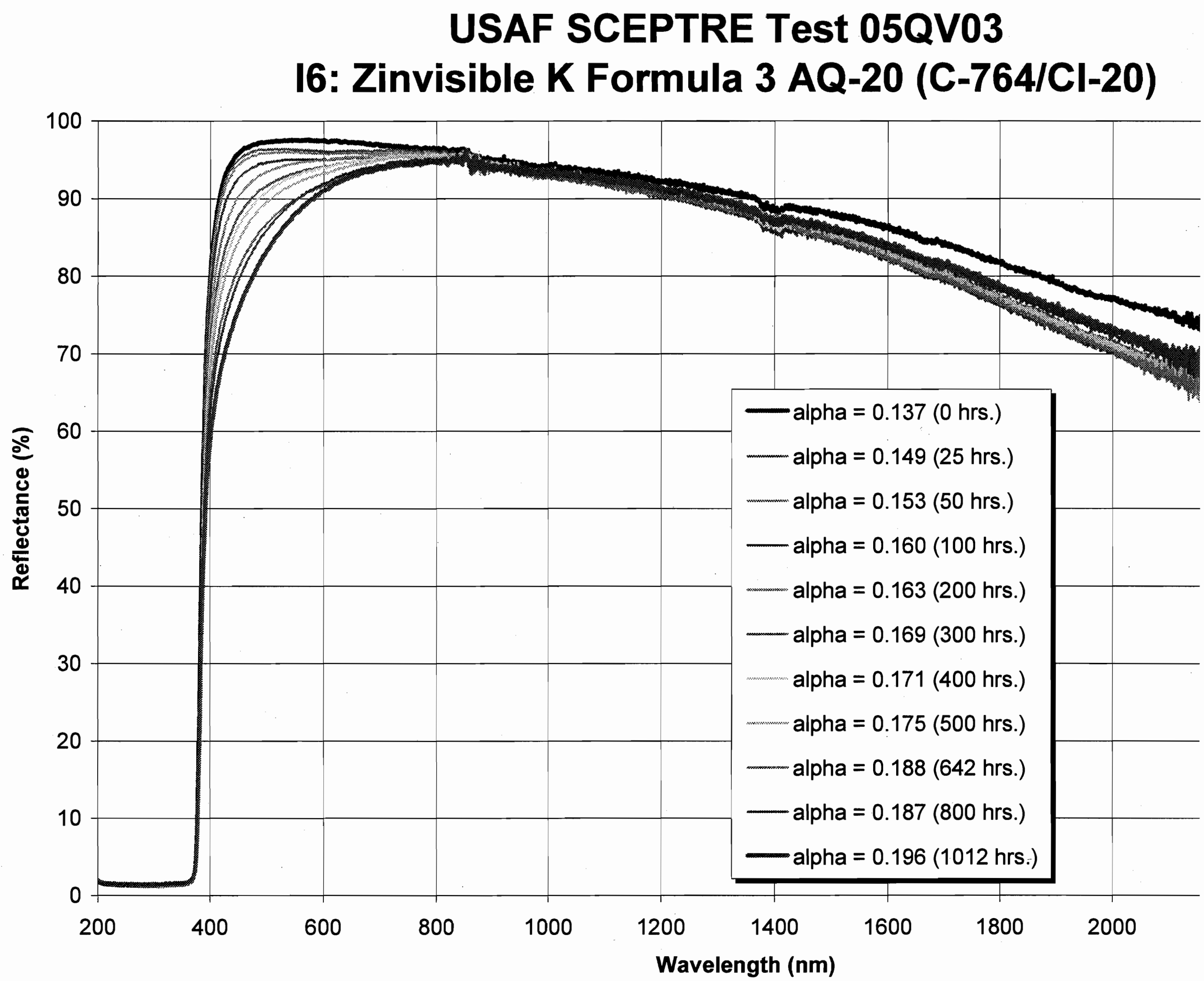


Figure A18. Spectral Reflectance History of Specimen I6: Zinvisible K Formula 3 AQ-20 (C-764/CI-20)

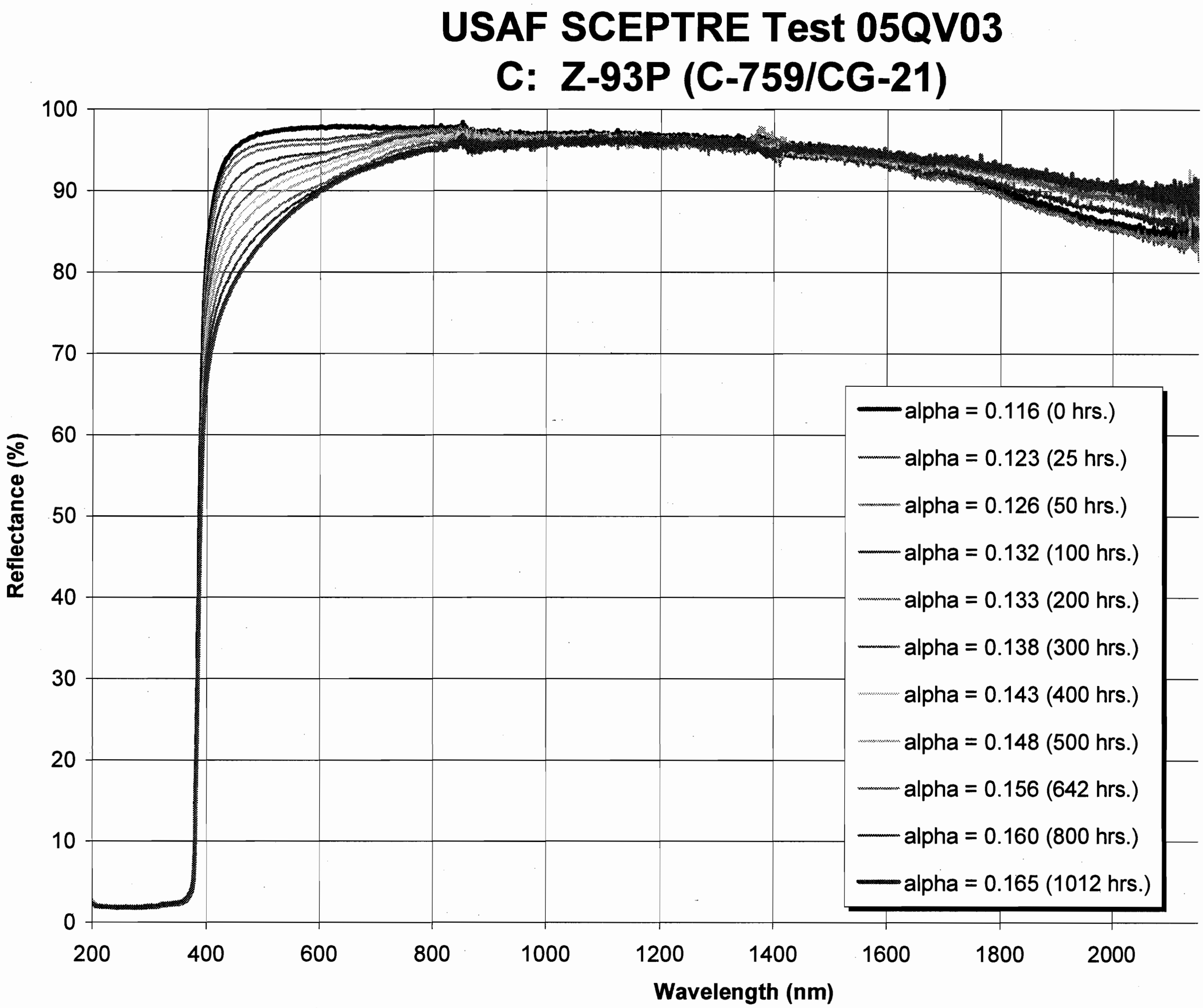


Figure A19. Spectral Reflectance History of Specimen C: Z-93P (C-759/CG-21)